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ABSTRACT:

PROBLEM TO BE SOLVED: To provide an extrusion forming apparatus and method, which can manufacture a thermoelectric material with higher thermoelectric performance by applying sufficient shear stress on a thermoelectric material.

SOLUTION: The extrusion forming apparatus 10 has a forming die 11 which comprises at least the first extrusion pass 15 with almost uniform cross section area and the second extrusion pass 17 connected to the first pass. The second extrusion pass 17 is bent at an angle more than 0 degree and less than 180 degree to the first extrusion pass 15 and has a zone whose cross section area is reduced toward an exit of formed material.

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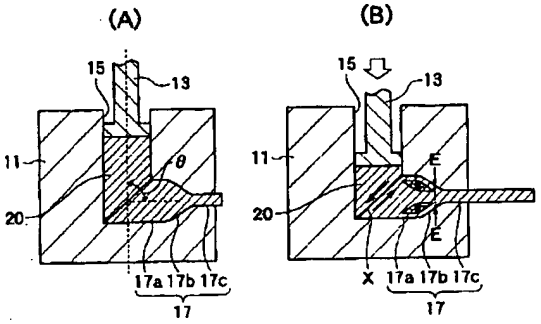
最終頁に続く

(54)【発明の名称】　押出し加工装置及び押出し加工方法

(57)【要約】
【課題】　熱電材料に十分なせん断応力を付加することにより、高い熱電性能をもつ熱電材料を製造できる押出し加工装置及び押出し加工方法を提供する。
【解決手段】　押出し成形加工装置１０は、ほぼ一定の断面積を有する第１の押出し経路１５と、第１の押出し経路に継続する第２の押出し経路１７とが少なくとも形成されたダイス１１を具備する。第２の押出し経路１７は、第１の押出し経路１５に対して０度より大きく１８０度より小さい角度を成し、材料の出口側に向かって断面積が減少する領域を有する。



1

【特許請求の範囲】

【請求項１】　材料の入口側に位置する第１の押出し経路と、

前記第１の押出し経路に継続する第２の押出し経路であって、前記第１の押出し経路に対して０度より大きく１８０度より小さい角度を成す前記第２の押出し経路と、が少なくとも形成されており、いずれかの押出し経路において、材料の出口側に向かって断面積が減少する領域を有するダイスを具備する押出し加工装置。

【請求項２】　材料の入口側に位置する第１の押出し経路と、前記第１の押出し経路に継続する第２の押出し経路であって、前記第１の押出し経路に対して０度より大きく１８０度より小さい角度を成す前記第２の押出し経路とが少なくとも形成されたダイスと、

前記第１の押出し経路に注入された材料を押すための押出し工具と、

前記第２の押出し経路から押し出される材料を押し返すための押さえ工具と、を具備する押出し加工装置。

【請求項３】　前記第１及び第２の押出し経路の各々が矩形断面を有することを特徴とする請求項１又は２記載の押出し加工装置。

【請求項４】　前記ダイスが複数の出口を有することを特徴とする請求項１～３のいずれか１項記載の押出し加工装置。

【請求項５】　第１の方向に設けられた材料の入口側に位置する第１の押出し経路と、

第２の方向に設けられた材料の入口側に位置する第２の押出し経路と、

前記第１及び第２の押出し経路に継続する第３の押出し経路であって、前記第１及び第２の押出し経路に対して０度より大きく１８０度より小さい角度を成す前記第３の押出し経路と、が少なくとも形成されたダイスを具備する押出加工装置。

【請求項６】　前記ダイスが、前記第３の押出し経路において、材料の出口側に向かって断面積が減少する領域を有する、請求項５記載の押出加工装置。

【請求項７】　前記第１の押出し経路に注入された材料を第１の方向から押すための第１の押出し工具と、

前記第２の押出し経路に注入された材料を第２の方向から押すための第２の押出し工具と、

前記第３の押出し経路から押し出される材料を押し返すための押さえ工具と、をさらに具備する請求項５記載の押出加工装置。

【請求項８】　前記第２の押出し経路が、前記第１の押出し経路と１８０度を成すことを特徴とする請求項５～７のいずれか１項記載の押出加工装置。

【請求項９】　請求項１～８のいずれか１項記載の押出し加工装置を用いて材料の押出し加工を行うことを特徴とする押出し加工方法。

【請求項１０】　請求項１記載の押出し加工装置を用いて、１回の加工ごとに材料の断面積を小さくしながら材料の押出し加工を複数回行うことを特徴とする押出し加工方法。

2

【請求項１１】　請求項１～４のいずれか１項記載の押出加工装置を用いて、材料の先端にダミー材を入れながら材料の押出し加工を複数回行うことを特徴とする押出し加工方法。

【請求項１２】　熱間で材料の押出し加工を行うことを特徴とする請求項９～１１のいずれか１項記載の押出し加工方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、一般的に、金属、半導体材料、酸化物等に対して塑性変形加工の一種である押出し加工を施すために用いられる押出し加工装置及び押出し加工方法に関し、特に、熱電素子を製造するために用いられる熱電材料の押出し加工に適した押出し加工装置及び押出し加工方法に関する。

【０００２】

【従来の技術】熱電素子とは、トムソン効果、ペルチェ効果、ゼーベック効果等の熱電効果を利用した素子、熱電対、電子冷却素子等をいい、構造が簡単かつ取扱いが容易で安定な特性を維持できることから、広範囲にわたる利用が注目されている。特に、電子冷却素子としては、局所冷却や室温付近の精密な温度制御が可能であることから、オプトエレクトロニクスや半導体レーザ等の温度調節、並びに、小型冷蔵庫等への適用に向けて、広く研究開発が進められている。

【０００３】熱電素子としては、比抵抗（抵抗率）ρ、熱伝導率κ、ゼーベック係数αを用いて、$Z=\alpha^2/\rho\kappa$で表される性能指数Ｚの大きなものが望まれる。また、熱電半導体材料の多くは、結晶構造に起因した異方性を有する。一般に、異方性結晶はへき開性を有し、材料強度が脆弱である。このため、実用材料としては、単結晶材料ではなく、性能指数の大きな結晶方位に配向させた多結晶材料が使用される。良好な性能指数を得るためには、凝固させた結晶材料を粉体化後に焼結し、焼結後にせん断応力を与える押出し加工等の塑性加工の工程を設けることが有効である。

【０００４】日本国特許出願公開（特開）２０００－１２４５１２号公報には、熱電半導体材料の配向度を高めると共に、直方体状の熱電素子を切り出す際の歩留まり率を高め、表面の研磨工程と圧密工程を可能とする熱電半導体材料の製造方法が開示されている。

【０００５】図１５は、特開２０００－１２４５１２号公報に開示されている熱電半導体材料の製造方法を模式的に説明する図であり、図１５の（Ａ）はパンチ押圧前、（Ｂ）はパンチ押圧後の状態を示している。この製造方法においては、熱電材料を直方体状の焼結体２１０とし、この焼結体２１０をダイス２１１に注入してパン

チ２１３を下降させる。ダイス２１１には、焼結体２１０が注入される入口側経路２１５と、入口側経路２１５より断面積の小さい直方体状の押出し経路２１７とが設けられている。パンチ２１３の下方向Ｄの押圧力により、焼結体２１０は押出し経路２１７から押し出され、直方体状の成形品が得られる。この押出しの際には、焼結体２１０が、ダイス２１１の側面方向Ｅから外力を受けて塑性変形する。このため、材料にかかる外力は大きく、かつ、材料全体に力がかかり易い。

【０００６】従って、この製造方法によれば、塑性変形による破壊と成形中の動的再結晶が良好に行われ、結晶粒が微細化する。この結晶粒の微細化により熱伝導率κが小さくなり、性能指数Ｚが向上する。また、熱間鍛造よりも外力の加わり度合いが良好であり、異方性が高まって性能指数が向上する。

【０００７】また、祝迫らによる文献「強せん断付加押し出しによるＢｉ－Ｔｅ系材料の配向制御」（第５１回塑性加工連合講演会、２０００年１１月３～５日）には、Ｌ字型の経路を有するダイスを用いて熱電材料に高いせん断応力を与えることにより、より完全な異方性の再発現を可能にすることが開示されている。

【０００８】図１６は、上記文献に開示されている方法を模式的に説明する図であり、図１６の（Ａ）はパンチ押圧前、（Ｂ）はパンチ押圧後の状態を示している。この方法においては、入口側経路２２５と出口側経路２２７とからなるＬ字型の経路を有するダイス２２１中にＢｉ－Ｔｅ系材料２２０を封入し、パンチ２２３により押圧する。材料２２０は、経路の直角部Ｘで強いせん断応力を受けながら押し出される。このとき、Ｂｉ－Ｔｅ結晶の容易すべり面（へき開面）ですべりが発生し、同時に回転を起こすことにより、結晶は再配列する。

【０００９】

【発明が解決しようとする課題】しかしながら、近年では、熱電素子が適用されるオプトエレクトロニクス、半導体レーザなどの高性能化や高速化にともなって、より性能の高い熱電素子の開発が進んでいる。さらに、この分野の発展により、熱電素子の効率的な大量生産も要求されている。

【００１０】上述の特開２０００－１２４５１２号公報に開示されている方法によれば、ダイス中の材料とダイスとの接触面近傍では十分なせん断応力が得られており結晶が再配列し易いが、図１５（Ｂ）に示す材料の中心部Ｃと側部Ｐとのせん断応力の差をなくすことにより、さらに均一な配向度を得ることが期待される。

【００１１】また、「強せん断付加押し出しによるＢｉ－Ｔｅ系材料の配向制御」に開示されている方法によれば、材料は断面中のどの部分をとっても均一にせん断応力を受けるため、材料の内部において特性が一様な製品が得られる。しかしながら、材料がせん断応力を受けるのは、ダイスの直角部（Ｌ字型部）Ｘを通過する際の１回だけである。このため、付加されるせん断応力の量が十分とはいえず、十分な配向が得られ難い。

【００１２】一方、従来の他の金属材料のＬ字押出しにおいては、ダイスの入口と出口の形状を同じにして複数回のＬ字押出しをすることによって、せん断応力を複数回付加することができる。しかし、Ｂｉ－Ｔｅ等の脆い脆性材料を用いる場合には、出口を入口より小さくすることにより、出口において圧縮応力を付加する必要がある。これは、入口と出口の形状を等しくすると、Ｌ字部で材料が破壊（座屈）してしまうためである。従って、熱電材料の成形においては、複数回のＬ字押出しを行うことができず、せん断応力を複数回付加することができない。

【００１３】そこで、上記の点に鑑み、本発明は、材料に十分なせん断応力を付加することにより、高い熱電性能をもつ熱電材料を製造できる押出し加工装置及び押出し加工方法を提供することを目的とする。

【００１４】

【課題を解決するための手段】以上の課題を解決するため、本発明の第１の観点に係る押出し加工装置は、材料の入口側に位置する第１の押出し経路と、第１の押出し経路に継続する第２の押出し経路であって、第１の押出し経路に対して０度より大きく１８０度より小さい角度を成す第２の押出し経路とが少なくとも形成されており、いずれかの押出し経路において、材料の出口側に向かって断面積が減少する領域を有するダイスを具備する。

【００１５】Ｌ字押出しに加えて、いずれかの押出し経路を絞り形状とすることによって、この部分でもせん断応力を付加することができる。従って、Ｌ字押出しと通常押出しのそれぞれの場合におけるせん断応力を加えることができるので、結晶粒がさらに微細化し、配向度が向上する。従来のＬ字押出しでは出口形状を小さくして材料の破壊（座屈）を防いでいたが、本発明の第１の観点によれば、最後の押出し経路を通常の押出し型のように絞り形状とすることによって、材料の破壊（座屈）を防ぐことができる。

【００１６】また、本発明の第２の観点に係る押出し加工装置は、材料の入口側に位置する第１の押出し経路と、第１の押出し経路に継続する第２の押出し経路であって、第１の押出し経路に対して０度より大きく１８０度より小さい角度を成す第２の押出し経路とが少なくとも形成されたダイスと、第１の押出し経路に注入された材料を押すための押出し工具と、第２の押出し経路から押し出される材料を押し返すための押さえ工具とを具備する。

【００１７】本発明の第２の観点によれば、ダイスの第２の押出し経路から押し出される材料を押し返す工具を備えることにより、材料の破壊（座屈）を防ぐことができる。また、第２の押出し経路から高い圧縮応力を付加

できるため、L字部でのせん断応力も高くなる。その後、押出しパンチ１３と押さえパンチ１４の動きを逆転させて往復させることにより、繰り返し押出しを行うこともできる。さらに、第１の押出し経路と第２の押出し経路の形状を同じにすることができるため、材料の繰り返し押出しが可能となる。従って、同一の装置を用いて、せん断応力を複数回付加することにより、結晶粒がさらに微細化し、配向度が向上する。

【００１８】以上において、第１及び第２の押出し経路の各々が矩形断面を有することが望ましい。断面を矩形とすることにより、ダイスの幅方向におけるせん断応力のバラツキをなくして、せん断応力を均一化することができる。また、ダイスが複数の出口を有するようにすれば、１度に複数の材料を製造することができるので量産に適している。

【００１９】また、本発明の第３の観点に係る押出し加工装置は、第１の方向に設けられた材料の入口側に位置する第１の押出し経路と、第２の方向に設けられた材料の入口側に位置する第２の押出し経路と、第１及び第２の押出し経路に継続する第３の押出し経路であって、第１及び第２の押出し経路に対して０度より大きく１８０度より小さい角度を成す第３の押出し経路とが少なくとも形成されたダイスを具備する。

【００２０】本発明の第３の観点によれば、第１及び第２の経路において熱電材料に両側から押し圧力をかけて第３の経路に押し出すので、熱電材料に左右対称のせん断応力が付加される。従って、熱電材料において、結晶粒の配向の対称性を向上させることができる。

【００２１】本発明に係る押出し加工方法は、上記のいずれかの押出し加工装置を用いて材料の押出し加工を行う。特に、本発明の第１の観点に係る押出し加工装置を用いる場合には、１回の加工ごとに材料の断面積を小さくしながら材料の押出し加工を複数回行うことにより、結晶粒をさらに微細化することが可能である。

【００２２】また、本発明の第１及び第２の観点に係る押出し加工装置を用いる場合には、材料の先端にダミー材を入れながら材料の押出し加工を複数回行うことが好ましい。特に、複数回Ｌ字押出しを行う際に、材料の破壊（座屈）を防ぐことができる。さらに、以上において、熱間で材料の押出し加工を行うことが望ましい。その場合には、材料が破壊し難くなり、再結晶が起こり易くなる。

【００２３】

【発明の実施の形態】以下、図面に基いて本発明の実施の形態について説明する。なお、同一の構成要素については同一の参照番号を付して、説明を省略する。図１は、本発明の第１の実施形態に係る押出し加工装置の概要を示す図である。図１に示すように、押出し加工装置１０は、粉末成形された熱電材料２０を押し出すパンチ（押出し工具）１３と、パンチ１３によって押し出される熱電材料２０を塑性変形させる金型であるダイス１１を含んでいる。パンチ１３は、例えば油圧アクチュエータ（油圧シリンダ）によって駆動されるスライド１によって上下動を行う。パンチ１３の押出し圧力は、荷重計２によって計測され、パンチ１３の変位は、変位計５によって計測される。変位計５の計測値と経過時間との関係をモニターすることにより、パンチ１３がほぼ一定の押出し速度で熱電材料２０を押し出すように、スライド１の駆動を制御することができる。

【００２４】ダイス１１が設置されているベース７の上には、ダイス１１及び熱電材料２０を加熱するためのヒータ６が設置されている。ヒータ６を用いることにより、熱間押出し加工を行うことが可能である。ダイス１１の温度は、ダイス１１の近傍に配置された温度センサ８によって計測される。温度センサ８の計測値をフィードバックしてヒータ６の発熱量を制御することにより、ダイス１１及び熱電材料２０を所望の温度に保つことができる。

【００２５】熱間押出し加工は、アルゴン等の不活性ガス雰囲気もしくは真空中で、加工温度を３５０℃～６００℃、より好ましくは４２０℃～５００℃程度に保ちながら、押出し速度を例えば０．１ｍｍ／ｍｉｎとして行うことが望ましい。なお、本実施形態においては、ダイス１１を固定してパンチ１３を移動させたが、この逆に、パンチ１３を固定してダイス１１を移動させてもかまわない。

【００２６】図２は、本発明の第１の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図であり、図２の（Ａ）と（Ｂ）は、押出し加工中の２つの状態を示している。ダイス１１には、パンチ１３が上下に出し入れされる入口側経路１５と、成形品が押し出される出口側経路１７とが形成されている。入口側経路１５と出口側経路１７は連通（継続）しており、入口側経路１５の長手方向の軸と出口側経路１７の長手方向の軸とが角度θを形成している。本発明においては、角度θが０°より大きく１８０°より小さい範囲にあることが必要であり、望ましくは４５～１３５°とする。以下の実施形態においては、角度θを約９０°としている。

【００２７】入口側経路１５は、四角形（より好ましくは矩形）の断面形状を有し、断面積は経路の長手方向においてほぼ一定である。出口側経路１７は、四角形（より好ましくは矩形）の断面形状を有し、ダイス１１の出口に向かって断面積が減少する領域を有するように形成されている。すなわち、出口側経路１７は、入口側経路１５との連通部１７ａと、断面積が徐々に減少する絞り部１７ｂと、断面積が減少したままの縮径部１７ｃとを含んでいる。なお、出口側経路１７の断面は、幅方向（紙面と垂直な方向）の寸法をほぼ一定として、図中の上下方向においてのみ絞りをかけることが望ましい。

【００２８】熱電素子の製造に使用される熱電材料としては、アンチモン、ビスマス、セレン、テルル、コバルト、マンガン、シリコン、亜鉛、マグネシウム、鉄、ゲルマニウム等、及びこれらを含む化合物が挙げられる。このような材料の溶製材、粉体、圧粉体、焼結体、及びこれらの加工体に対して、押出し加工が行われる。

【００２９】さらに詳しく説明すると、例えば、Ｖ族元素としてアンチモン（Ｓｂ）やビスマス（Ｂｉ）を用い、ＶＩ族元素としてセレン（Ｓｅ）やテルル（Ｔｅ）を用いる。Ｖ族元素とＶＩ族元素の固溶体は、六方晶構造を有する。熱電材料の具体的な組成については、Ｐ型素子の材料として、テルル化ビスマス（Bi_2Te_3）とテルル化アンチモン（Sb_2Te_3）との混晶系固溶体にＰ型のドーパントを添加して用いたり、Ｎ型素子の材料として、テルル化ビスマス（Bi_2Te_3）とセレン化ビスマス（Bi_2Se_3）との混晶系固溶体にＮ型のドーパントを添加して用いることができる。

【００３０】ダイス１１を用いて熱電材料２０の押出し加工する際には、熱電材料２０を入口側経路１５に注入し、パンチ１３を下降させると、出口側経路１７から成形品が押し出される。このとき、図２（Ｂ）に示すように、焼結体２０には、様々なせん断応力が付加される。入口側経路１５と出口側経路１７がほぼ直角に連通する境界部Ｘがせん断帯となり、境界部Ｘにおいて熱電材料２０は強いせん断応力を受ける。

【００３１】さらに、熱電材料２０が出口側経路１７に進むと、同径路の絞り部１７ｂの側面方向Ｅから外力を受け、熱電材料２０が塑性変形する。従って、Ｌ字押出しと通常押出しのそれぞれの場合におけるせん断応力を加えることができるので、結晶粒がさらに微細化し、配向度が向上する。特に、径路の断面を矩形とすることにより、ダイスの幅方向におけるせん断応力のバラツキをなくして、せん断応力を均一化することができる。また、ダイス１１の出口側の形状は、上述のように絞り形状となっているので、ダイス１１の出口から加工を受けて出てくる材料を拘束し、材料の破壊（座屈）を防ぐことができる。

【００３２】次に、本発明の第２の実施形態について説明する。図３は、本発明の第２の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図であり、図３の（Ａ）はパンチ押圧前、（Ｂ）はパンチ押圧後の状態を示している。

【００３３】本実施形態に係る押出し加工装置は、２つのパンチ１３、１４を備えている。ダイス２１には、パンチ１３が上下に出し入れされる入口側経路２５と、パンチ１４が左右に出し入れされる出口側経路２７とが形成されている。ダイス２１において、入口側経路２５と出口側経路２７は連通している。入口側経路２５と出口側経路２７は、同じ四角形（より好ましくは矩形）の断面形状を有し、それぞれの経路の断面積は長手方向においてほぼ一定であることが望ましい。入口側経路２５には、同径路に注入された材料を押すための押出しパンチ（押出し工具）１３が、同経路をスライドするように設けられている。また、出口側経路２７には、同径路から押し出される材料を押し返すことにより背圧をかける押さえパンチ（押さえ工具）１４が、同経路をスライドするように設けられている。

【００３４】ダイス２１を用いて熱電材料の押出し加工する際には、入口側経路２５に熱電材料を注入し、押出しパンチ１３を下降させるとともに、押さえパンチ１４を背圧をかけながら後退させる。このとき、図３（Ｂ）に示すように、熱電材料２０には、様々なせん断応力が付加される。すなわち、第１の実施形態と同様に、入口側経路２５と出口側経路２７がほぼ直角に連通する境界部Ｘがせん断帯となり、境界部Ｘにおいて熱電材料２０は強いせん断応力を受ける。さらに、熱電材料２０は、出口側経路２７において押さえパンチ１４から高い圧縮応力Ｓを受けているため、境界部Ｘでのせん断応力が強くなる。その後、押出しパンチ１３と押さえパンチ１４の動きを逆転させて往復させることにより、繰り返し押出しを行うこともできる。

【００３５】また、本実施形態においては、入口側経路２５と出口側経路２７の断面形状を同じにすることにより、材料の繰り返し押出しが可能となる。その場合には、材料に複数回せん断応力を付加することができるので、結晶粒がさらに微細化し、配向度が向上する。

【００３６】次に、本発明の第３の実施形態について説明する。図４は、本発明の第３の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図であり、図４の（Ａ）と（Ｂ）は、押出し加工中の２つの状態を示している。

【００３７】本実施形態に係る押出し加工装置は、第２の実施形態における２つのパンチの形状を変更したものである。押出しパンチ２３は、その押出し面が、ダイス２１の境界部Ｘにおける熱電材料２０のせん断面とほぼ平行を保ちながら、入口側経路２５をスライドする。また、押さえパンチ２４は、ダイス２１の境界部Ｘにおける熱電材料２０のせん断面とほぼ平行を保ちながら、出口側経路２７をスライドする。これにより、押出し力の方向を材料の移動方向と一致させて、よりスムーズな押出し加工を行うことができる。

【００３８】なお、本実施形態においては、焼結された熱電材料のバルクを斜めに切り出すことにより押出し加工用の熱電材料２０を作成し、結晶のへき開面がダイス２１の境界部Ｘにおけるせん断面とほぼ平行となるようにして押出し加工を行うことが望ましい。

【００３９】次に、本発明の第４の実施形態について説明する。図５は、本発明の第４の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。ダイス３１には、パンチ３３が上下に

出し入れされる入口側経路３５と、成形品が押し出される出口側経路３７とが形成されている。ダイス３１において、入口側経路３５と出口側経路３７は連通している。

【００４０】入口側経路３５は、四角形（より好ましくは矩形）の断面形状を有し、出口側経路３７との連通部に向かって断面積が減少する領域を有するように形成されている。すなわち、入口側経路３５は、断面積がほぼ一定の入口部３５ａと、断面積が徐々に減少する絞り部３５ｂと、断面積が減少したままの縮径部３５ｃとを含んでいる。出口側経路３７は、四角形（より好ましくは矩形）の断面形状を有し、断面積は経路の長手方向においてほぼ一定である。なお、入口側経路３５の断面は、幅方向（紙面と垂直な方向）の寸法をほぼ一定として、図中の上下方向においてのみ絞りをかけることが望ましい。

【００４１】ダイス３１を用いて熱電材料の押出し加工する際には、熱電材料２０を入口側経路３５に注入し、パンチ３３を下降させると、出口側経路３７から成形品が押し出される。このとき、入口側経路３５の絞り部３５ｂの側面方向から外力を受け、熱電材料２０が塑性変形する。さらに、熱電材料２０が出口側経路３７に進むと、入口側経路３５と出口側経路３７がほぼ直角に連通する境界部Ｘがせん断帯となり、境界部Ｘにおいて熱電材料２０は強いせん断応力を受ける。従って、通常押出しとＬ字押出しのそれぞれの場合におけるせん断応力を加えることができるので、結晶粒がさらに微細化し、配向度が向上する。特に、断面を矩形とすることにより、ダイスの幅方向におけるせん断応力のバラツキをなくして、せん断応力を均一化することができる。

【００４２】次に、本発明の第５の実施形態について説明する。図６は、本発明の第５の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。ダイス４１には、パンチ３３が上下に出し入れされる入口側経路４５と、成形品が押し出される出口側経路４７とが形成されている。ダイス４１において、入口側経路４５と出口側経路４７は連通している。

【００４３】入口側経路４５は、四角形（より好ましくは矩形）の断面形状を有し、出口側経路４７との連通部に向かって断面積が減少する領域を有するように形成されている。すなわち、入口側経路４５は、断面積がほぼ一定の入口部４５ａと、断面積が徐々に減少する絞り部４５ｂとを含んでいる。出口側経路４７は、四角形（より好ましくは矩形）の断面形状を有し、ダイス４１の出口に向かって断面積が減少する領域を有するように形成されている。すなわち、出口側経路４７は、入口側経路４５との連通部４７ａと、断面積が徐々に減少する絞り部４７ｂと、断面積が減少したままの縮径部４７ｃとを含んでいる。なお、入口側経路４５及び出口側経路４７の断面は、幅方向（紙面と垂直な方向）の寸法をほぼ一定として、図中の上下方向においてのみ絞りをかけることが望ましい。

【００４４】ダイス４１を用いて熱電材料の押出し加工する際には、熱電材料２０を入口側経路４５に注入し、パンチ３３を下降させると、出口側経路４７から成形品が押し出される。このとき、入口側経路４５の絞り部４５ｂの側面方向から外力を受け、熱電材料２０が塑性変形する。さらに、熱電材料２０が出口側経路４７に進むと、入口側経路４５と出口側経路４７がほぼ直角に連通する境界部Ｘがせん断帯となり、熱電材料２０は、強いせん断応力を受ける。加えて、出口側経路４７の絞り部４７ｂの側面方向から外力を受け、熱電材料２０が塑性変形する。

【００４５】従って、Ｌ字押出しと２回分の通常押出しのそれぞれの場合におけるせん断応力を加えることができるので、結晶粒がさらに微細化し、配向度が向上する。特に、断面を矩形とすることにより、ダイスの幅方向におけるせん断応力のバラツキをなくして、せん断応力を均一化することができる。また、ダイス４１の出口側の形状は、上述のように絞り形状となっているので、ダイス４１の出口から加工を受けて出てくる材料を拘束して、材料の破壊（座屈）を防ぐことができる。

【００４６】次に、本発明の第６の実施形態について説明する。図７は、本発明の第６の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。本実施形態に係る押出し加工装置のダイス５１には、パンチ１３が上下に出し入れされる入口側経路５５と、成形品が押し出される２つの出口側経路５７、５８とが形成されている。入口側経路５５と出口側経路５７、５８は連通しており、出口側経路５７、５８は、入口側経路５５に対してそれぞれ約９０°の角度を成し、互いに反対方向に延びている。また、出口側経路５７、５８は、第１の実施形態と同様に、ダイスの出口に向かって断面積が減少するように形成されている。

【００４７】入口側経路５５に熱電材料２０を注入し、パンチ１３を下降させると、２つの出口側経路５７、５８から成形品が押し出される。このとき、入口側経路５５と２つの出口側経路５７、５８とがほぼ直角に連通する２つの境界部Ｘ、Ｙはせん断帯となり、熱電材料２０にせん断応力が付加される。

【００４８】なお、本実施形態においては２つの出口側経路５７、５８を入口側経路５５に対してそれぞれ約９０°の角度を成すように設けたが、出口側経路は３つ以上設けても良い。また、入口側経路と出口側経路との成す角度は、０°より大きく１８０°より小さい範囲にあれば良く、特に４５°～１３５°の範囲が望ましい。

【００４９】次に、本発明の第７の実施形態について説明する。図８は、本発明の第７の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側

面断面図である。本実施形態に係る押出し加工装置は、３つのパンチ１２、１３、１４を備えている。ダイス６１には、パンチ１３が上下に出し入れされる入口側経路６５と、パンチ１２が左右に出し入れされる出口側経路６７と、パンチ１４が左右に出し入れされる出口側経路６８とが形成されている。ダイス６１において、入口側経路６５と出口側経路６７、６８は連通している。入口側経路６５には、同径路に注入された材料を押すための押出しパンチ（押出し工具）１３が、同経路をスライドするように設けられている。また、出口側経路６７には、同径路から押し出される材料を押し返すことにより背圧をかける押さえパンチ（押さえ工具）１２が、同経路をスライドするように設けられている。同様に、出口側経路６８には、同径路から押し出される材料を押し返すことにより背圧をかける押さえパンチ１４が、同経路をスライドするように設けられている。

【００５０】ダイス６１を用いて熱電材料の押出し加工する際には、入口側経路６５に熱電材料を注入し、押出しパンチ１３を下降させるとともに、押さえパンチ１２、１４を背圧をかけながら後退させる。このとき、入口側経路６５と２つの出口側経路６７、６８とがほぼ直角に連通する２つの境界部Ｘ、Ｙはせん断帯となり、熱電材料２０にせん断応力が付加される。さらに、熱電材料２０は、出口側経路６７、６８において押さえパンチ１２、１４から高い圧縮応力を受けているため、境界部Ｘ、Ｙでのせん断応力が強くなる。

【００５１】次に、本発明の第８の実施形態について説明する。図９は、本発明の第８の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。本実施形態に係る押出し加工装置のダイス７１には、パンチ１３が上下に出し入れされる入口側経路７５と、成形品が押し出される出口側経路７７と、入口側経路７５と出口側経路７７とを接続する中間経路７６とが形成されている。各経路は連通しており、入口側経路７５と中間経路７６のなす角度は約９０°であり、中間経路７６と出口側経路７７のなす角度は約９０°である。各経路の断面形状は、四角形（より好ましくは矩形）である。また、入口側経路７５の断面積と中間経路７６の断面積とは等しい。出口側経路７７は、ダイス７１の出口に向かって断面積が減少するように形成されている。即ち、出口側経路７７は、中間経路７６との連通部から断面積が徐々に減少する絞り部７７ａと、断面積が減少したままの縮径部７７ｂとを含んでいる。

【００５２】入口側経路７５に熱電材料を注入し、パンチ１３を下降させると、焼結体は中間経路７６を通って出口側経路７７から押し出される。このとき、連通する経路内には、入口側経路７５と中間経路７６が直角に連通する境界部Ｘ、及び、中間経路７６と出口側経路７７が直角に連通する境界部Ｙの２ヶ所において、熱電材料２０に強いせん断帯が付加される。さらに、出口側経路７７には絞り部７７ａが形成されているため、この絞り部７７ａにおいても側面方向Ｅから外力を受け、熱電材料２０が塑性変形する。従って、結晶粒をさらに微細化させ、配向性を高めることが可能である。また、ダイス７１の出口側の形状は、上述のように絞り形状となっているので、ダイス７１の出口から加工を受けて出てくる材料を拘束して、材料の破壊（座屈）を防ぐことができる。

【００５３】次に、本発明の第９の実施形態について説明する。図１０は、本発明の第９の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。本実施形態に係る押出し加工装置のダイス８１には、パンチ１３が上下に出し入れされる入口側経路８５と、成形品が押し出される出口側経路８７と、入口側経路８５と出口側経路８７とを接続する中間経路８６とが形成されている。各経路は連通しており、入口側経路８５と中間経路８６のなす角度は約９０°であり、中間経路８６と出口側経路８７のなす角度は約９０°である。各経路の断面形状は、四角形（より好ましくは矩形）である。また、各経路の断面積は、入口側経路８５、中間経路８６、出口側経路８７の順に小さくなっている。さらに、出口側経路８７は、ダイス８１の出口に向かって断面積が減少するように形成されている。

【００５４】入口側経路８５に熱電材料２０を注入し、パンチ１３を下降させると、焼結体は中間経路８６を通って出口経路８７から押し出される。このとき、これらの経路は材料の出口側に向かうに従って断面積が減少しているため、材料の座屈を防ぐのに大変効果的である。

【００５５】特に、第８の実施形態又は第９の実施形態におけるように、押出し経路が複数の湾曲部をもつ場合には、熱電材料２０の先端にダミー材を入れて押出し加工を行うことにより、材料の破壊を抑えることができる。

【００５６】次に、本発明の第１０の実施形態について説明する。以下の実施形態においては、２つのパンチを用いてＴ字押出しを行う。図１１は、本発明の第１０の実施形態に係る押出し加工装置の概要を示す図である。図１１に示すように、押出し加工装置１００は、粉末成形された熱電材料２０を押し出す２つのパンチ１１２、１１３と、パンチ１１２、１１３によって押し出される熱電材料２０を塑性変形させる金型であるダイス１１１とを含んでいる。パンチ１１２、１１３は、例えば油圧アクチュエータ（油圧シリンダ）によって駆動されるスライド１０１、１０２によって左右に移動する。パンチ１１２、１１３の押出し圧力は、荷重計１０３、１０４によってそれぞれ計測され、パンチ１１２、１１３の変位は、変位計１０５、１０６によってそれぞれ計測される。変位計１０５、１０６の計測値と経過時間との関係をモニターすることにより、パンチ１１２、１１３がほぼ一定の押出し速度で熱電材料２０を押し出すように、

スライド101、102の駆動を制御することができる。

【0057】ダイス111が設置されているベース107の上には、ダイス111及び熱電材料20を加熱するためのヒータ108が設置されている。ヒータ108を用いることにより、熱間押出し加工を行うことが可能である。ダイス111の温度は、ダイス111の近傍に配置された温度センサ109によって計測される。温度センサ109の計測値をフィードバックしてヒータ108の発熱量を制御することにより、ダイス111及び熱電材料20を所望の温度に保つことができる。

【0058】熱間押出し加工は、アルゴン等の不活性ガス雰囲気もしくは真空中で、加工温度を350℃～600℃、より好ましくは420℃～500℃程度に保ちながら、押出し速度を例えば0．1mm／minとして行うことが望ましい。

【0059】図12は、本発明の第10の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。本実施形態に係る押出し加工装置のダイス111には、2つのパンチ112、113が左右にそれぞれ出し入れされる2つの入口側経路121、122と、成形品が押し出される出口側経路123とが形成されている。入口側経路112、113と出口側経路123は連通している。本発明においては、出口側経路123が、入口側経路112及び113に対して0°より大きく180°より小さい角度を成すことが必要であり、望ましくは45°～135°とする。以下の実施形態においては、この角度を約90°とし、また、入口側経路112と113とが成す角を約180°としている。

【0060】入口側経路121又は122から熱電材料20を注入し、パンチ112及び113を駆動すると、熱電材料20は両側から均等に加圧され、出口側経路123から成形品が押し出される。このとき、2つの入口側経路121、122と出口側経路123とがほぼ直角に連通する2つの境界部X、Yはせん断帯となり、熱電材料20にせん断応力が付加される。このように、左右から均等にせん断応力を付加することにより、熱電材料における結晶粒の配向が、熱電材料の中心面に対して左右対称となる。

【0061】次に、本発明の第11の実施形態について説明する。図13は、本発明の第11の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。本実施形態に係る押出し加工装置のダイス130には、2つのパンチ112、113が左右にそれぞれ出し入れされる入口側経路131、132と、成形品が押し出される2つの出口側経路133とが形成されている。出口側経路133には、第1の実施形態と同様に、ダイスの出口に向かって断面積が減少するように、絞り部134が形成されている。

【0062】入口側経路131又は132に熱電材料20を注入し、パンチ112及び113を駆動すると、熱電材料20は両側から均等に加圧され、出口側経路133から成形品が押し出される。このとき、2つの入口側経路131、132と出口側経路133とがほぼ直角に連通する2つの境界部X、Yはせん断帯となり、熱電材料20にせん断応力が付加される。さらに、熱電材料20が出口側経路133に進むと、同径路の絞り部134の側面方向Eから外力を受け、熱電材料20が塑性変形する。これにより、熱電材料を構成する結晶粒がさらに微細化し、配向度が向上する。

【0063】本実施形態によれば、T字押出しと通常押出しとの両方により、熱電材料の中心線に対して左右対称なせん断応力を受ける。従って、熱電材料の内部全体に渡って、粒界の配向が左右対称であり、位置による組織の特性にバラツキがない熱電材料を製造することができる。

【0064】次に、本発明の第12の実施形態について説明する。図14は、本発明の第12の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。本実施形態に係る押出し加工装置は、3つのパンチ112、113、114を備えている。ダイス140には、2つのパンチ112、113が左右にそれぞれ出し入れされる入口側経路141、142と、パンチ114が上下に出し入れされる出口側経路143とが形成されている。入口側経路141、142には、同径路に注入された材料を両側から押すための押出しパンチ112、113が、同経路をスライドするように設けられている。また、出口側経路67には、同径路から押し出される材料を押し返すことにより背圧をかける押さえパンチ（押さえ工具）114が、同経路をスライドするように設けられている。

【0065】ダイス140を用いて熱電材料の押出し加工する際には、入口側経路141又は142から熱電材料を注入し、押出しパンチ112及び113を駆動させるとともに、押さえパンチ114を背圧をかけながら後退させる。このとき、2つの入口側経路141、142と出口側経路143とがほぼ直角に連通する2つの境界部X、Yはせん断帯となり、熱電材料20にせん断応力が付加される。さらに、熱電材料20は、出口側経路143において押さえパンチ114から高い圧縮応力を受けているため、境界部X、Yでのせん断応力が強くなる。

【0066】

【発明の効果】以上述べた様に、本発明によれば、L字押出しと通常押出しのそれぞれの場合におけるせん断応力を加えることができるので、結晶粒をさらに微細化し、配向度を向上させることができる。この結晶粒の微細化により熱伝導率κが小さくなり、性能指数Zが向上する。また、配向度の向上によっても性能指数Zが向上

する。従って、高い熱電性能をもつ熱電材料を製造することが可能となる。また、Ｔ字押出しによりせん断応力を加える場合には、結晶粒を微細化すると共に、押出し方向に対して左右対称な配向性を有し、位置による組織の特性にバラツキがない、均質な熱電材料を製造することが可能となる。

【図面の簡単な説明】

【図１】本発明の第１の実施形態に係る押出し加工装置の概要を示す図である。

【図２】本発明の第１の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図であり、（Ａ）と（Ｂ）は、押出し加工中の２つの状態を示している。

【図３】本発明の第２の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図であり、（Ａ）はパンチ押圧前、（Ｂ）はパンチ押圧後の状態を示している。

【図４】本発明の第３の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図であり、（Ａ）と（Ｂ）は、押出し加工中の２つの状態を示している。

【図５】本発明の第４の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

【図６】本発明の第５の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

【図７】本発明の第６の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

【図８】本発明の第７の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

【図９】本発明の第８の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

【図１０】本発明の第９の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

【図１１】本発明の第１０の実施形態に係る押出し加工装置の概要を示す図である。

【図１２】本発明の第１０の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

【図１３】本発明の第１１の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

【図１４】本発明の第１２の実施形態に係る押出し加工装置において用いるダイスとパンチの構造を示す側面断面図である。

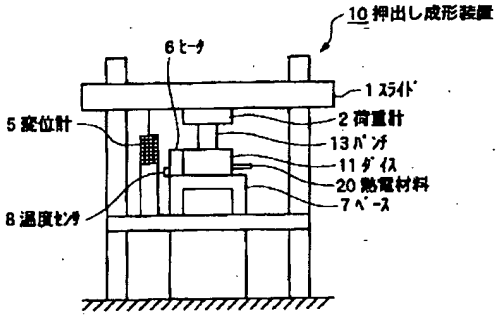
【図１５】特開２０００－１２４５１２号公報に開示されている熱電半導体材料の製造方法を模式的に説明する図であり、（Ａ）はパンチ押圧前、（Ｂ）はパンチ押圧後の状態を示している。

【図１６】文献「強せん断付加押し出しによるＢｉ－Ｔｅ系材料の配向制御」に開示されている方法を模式的に説明する図であり、（Ａ）はパンチ押圧前、（Ｂ）はパンチ押圧後の状態を示している。

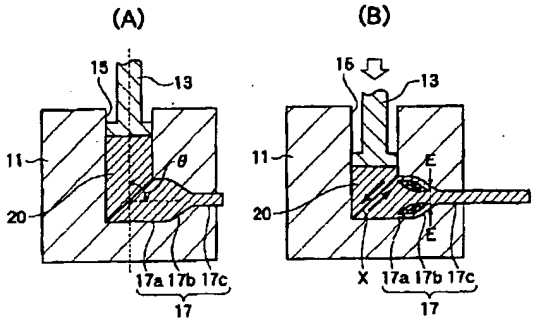
【符号の説明】

１、１０１、１０２　スライド
２、１０３、１０４　荷重計
５、１０５、１０６　変位計
６、１０８　ヒータ
７、１０７　ベース
８、１０９　温度センサ
１０、１００　押出し加工装置
１１、２１、３１、４１、５１、６１、７１、８１　ダイス
１２、１３、１４、２３、２４、３３　パンチ
１５、２５、３５、４５、５５、６５、７５、８５　入口側経路
７６、８６　中間経路
１７、２７、３７、４７、５７、５８、６７、６８、７７、８７　出口側経路
２０　熱電材料
１１１、１３０、１４０　ダイス
１１２、１１３、１１４　パンチ
１２１、１２２、１３１、１４２、１４１、１４２　入口側経路
１２３、１３３、１４３　出口側経路
１３４　絞り部

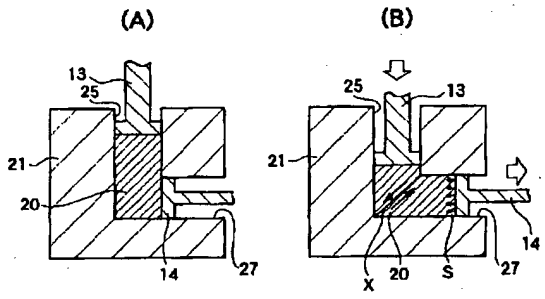
【図1】



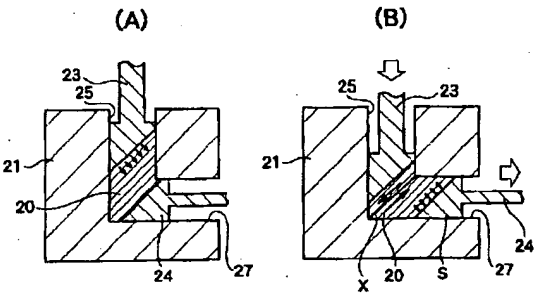
【図2】



【図3】



【図4】



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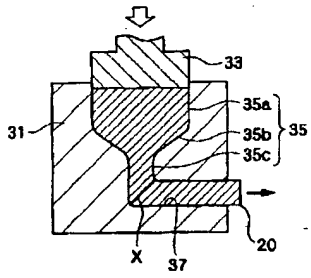

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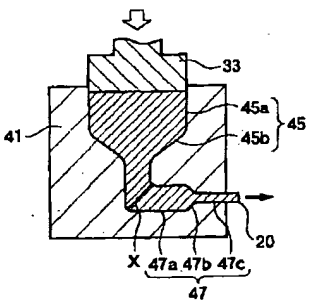

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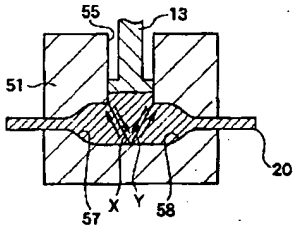

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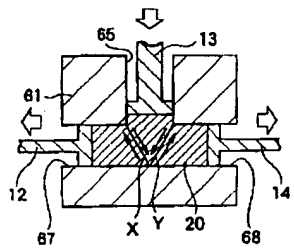

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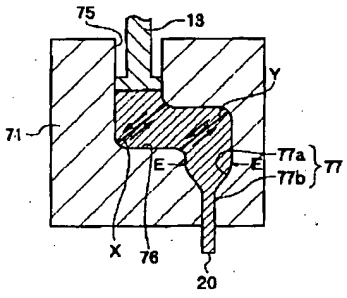

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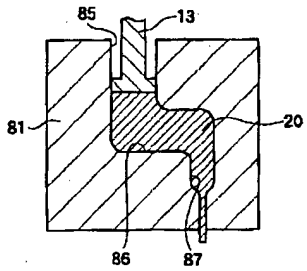

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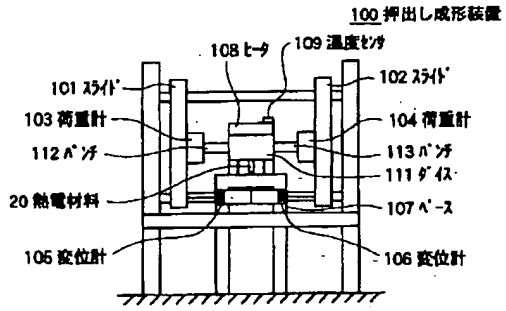

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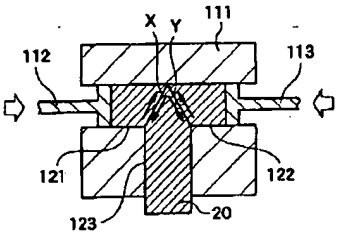

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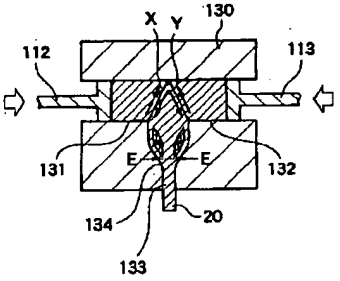

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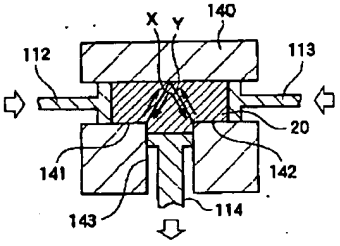

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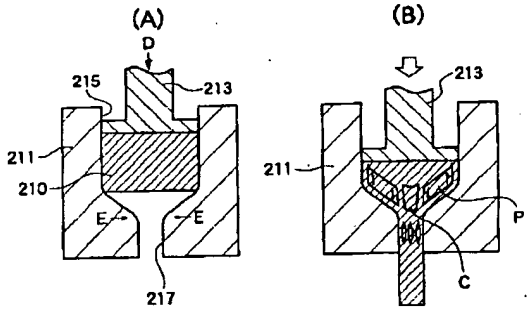

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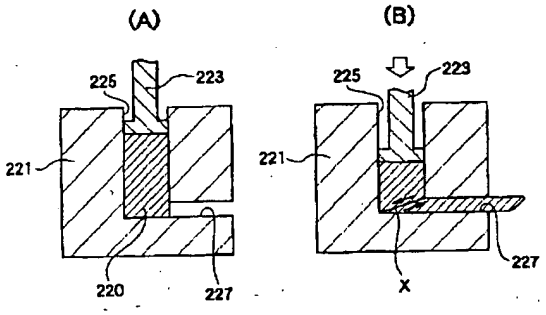

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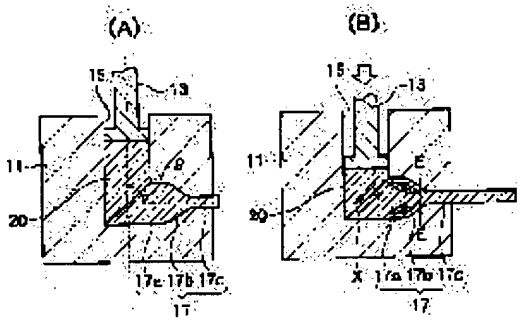
(54) APPARATUS AND METHOD FOR EXTRUSION FORMING

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an extrusion forming apparatus and method, which can manufacture a thermoelectric material with higher thermoelectric performance by applying sufficient shear stress on a thermoelectric material.
SOLUTION: The extrusion forming apparatus 10 has a forming die 11 which comprises at least the first extrusion pass 15 with almost uniform cross section area and the second extrusion pass 17 connected to the first pass. The second extrusion pass 17 is bent at an angle more than 0 degree and less than 180 degree to the first extrusion pass 15 and has a zone whose cross section area is reduced toward an exit of formed material.



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* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] Extruding equipment characterized by providing the following. The 1st extrusion path located in the entrance side of material. The extrusion path of the above 2nd of being the 2nd extrusion path continued for the extrusion path of the above 1st, and accomplishing a larger angle smaller than 180 degrees than 0 times to the extrusion path of the above 1st. ** -- the dice which is formed even if few, and has the field where the cross section decreases toward the outlet side of material in one of extrusion paths
[Claim 2] The 2nd extrusion path continued for the 1st extrusion path which is characterized by providing the following, and which is located in the entrance side of material, and the extrusion path of the above 1st. The dice with which the extrusion path of the above 2nd of accomplishing a larger angle smaller than 180 degrees than 0 times to the extrusion path of the above 1st was formed at least. The extrusion tool for pushing the material poured into the extrusion path of the above 1st, and the presser-foot tool for pushing back the material extruded from the extrusion path of the above 2nd.
[Claim 3] Extruding equipment according to claim 1 or 2 characterized by each of the above 1st and the 2nd extrusion path having a rectangle cross section.
[Claim 4] Extruding equipment of a claim 1-3 given in any 1 term with which the aforementioned dice is characterized by having two or more outlets.
[Claim 5] The 3rd extrusion path continued for the 1st extrusion path located in the entrance side of the material prepared in the 1st direction characterized by providing the following, the 2nd extrusion path located in the entrance side of the material prepared in the 2nd direction, and the above 1st and the 2nd extrusion path. The extrusion path of the above 3rd of accomplishing a larger angle smaller than 180 degrees than 0 times to the above 1st and the 2nd extrusion path. ** -- the dice formed even if few
[Claim 6] Extrusion equipment according to claim 5 with which the aforementioned dice has the field where the cross section decreases toward the outlet side of material in the extrusion path of the above 3rd.
[Claim 7] Extrusion equipment according to claim 5 which possesses further the 1st extrusion tool for pushing the material poured into the extrusion path of the above 1st from the 1st direction, the 2nd extrusion tool for pushing the material poured into the extrusion path of the above 2nd from the 2nd direction, and the presser-foot tool for pushing back the material extruded from the extrusion path of the above 3rd.
[Claim 8] Extrusion equipment of a claim 5-7 given in any 1 term with which the extrusion path of the above 2nd is characterized by accomplishing the extrusion path of the above 1st, and 180 degrees.
[Claim 9] The extruding method characterized by performing extruding of material using the extruding equipment of a claim 1-8 given in any 1 term.
[Claim 10] The extruding method characterized by performing extruding of material two or more times using extruding equipment according to claim 1, making the cross section of material small for every one processing.
[Claim 11] The extruding method characterized by performing extruding of material two or more times using the extrusion equipment of a claim 1-4 given in any 1 term, putting in dummy material at the nose of cam of material.
[Claim 12] The extruding method of the claim 9-11 characterized by performing extruding of material between heat given in any 1 term.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the extruding equipment suitable for extruding of the thermoelectric material used in order to manufacture a thermoelement especially, and the extruding method about the extruding equipment and the extruding method which are used in order to perform extruding which is a kind of plastic deformation processing to a metal, a semiconductor material, an oxide, etc. generally.
[0002]
[Description of the Prior Art] A thermoelement means the element using the thermoelectric effects, such as the Thomson effect, a Peltier effect, and the Seebeck effect, a thermocouple, an electronic cooling element, etc., and far-reaching use attracts attention from a property that handling is simply [structure] easy and stable being maintainable. Especially as an electronic cooling element, since the precise temperature control a local hypothermia and near a room temperature is possible, research and development are widely furthered towards the application to temperature control, such as optoelectronics and semiconductor laser, a small refrigerator, etc.
[0003] A big thing of the performance index Z expressed with 2/[of Z=alpha] rhokappa is desired using specific resistance (resistivity) rho, thermal conductivity kappa, and Seebeck-coefficient alpha as a thermoelement. Moreover, many of thermoelectrical semiconductor materials have an anisotropy resulting from the crystal structure. Generally, an anisotropy crystal has cleavage and its material strength is brittle. For this reason, as a charge of real material, not single crystal material but the polycrystal material which carried out orientation to the big crystal orientation of a performance index is used. In order to obtain a good performance index, it is effective to establish the process of plastic working, such as extruding which sinters the crystal material made to solidify after fine-particles-izing, and gives shearing stress after sintering.
[0004] While raising the amount of preferred orientation of a thermoelectrical semiconductor material to the Japan patent application public presentation (provisional publication of a patent) No. 124512 [2000 to] official report, the rate of the yield at the time of starting a rectangular parallelepiped-like thermoelement is raised, and the manufacture method of the thermoelectrical semiconductor material which makes a surface-lapping process and a consolidation process possible is indicated.
[0005] Drawing 15 is drawing which explains typically the manufacture method of the thermoelectrical semiconductor material currently indicated by JP,2000-124512,A, and, in (A) of drawing 15 , (B) shows the state after punch press before punch press. In this manufacture method, thermoelectric material is used as the rectangular parallelepiped-like sintered compact 210, this sintered compact 210 is poured into a dice 211, and punch 213 is dropped. The entrance-side path 215 into which a sintered compact 210 is poured, and the extrusion path 217 of the shape of a rectangular parallelepiped with the cross section smaller than the entrance-side path 215 are formed in the dice 211. A sintered compact 210 is extruded from the extrusion path 217 by the press force of punch 213 down [D], and rectangular parallelepiped-like mold goods are obtained according to it. In the case of this extrusion, a sintered compact 210 deforms [of a dice 211 / E] plastically in response to external force from the side. For this reason, the external force concerning material is large, and tends to require the force for the whole material.
[0006] Therefore, according to this manufacture method, dynamic recrystallization under destruction by plastic deformation and fabrication is performed good, and crystal grain makes it detailed. Thermal conductivity kappa becomes small by detailed-ization of this crystal grain, and a performance index Z improves. Moreover, rather than hot forging, external force is added, a degree is good, an anisotropy increases and a performance index improves.
[0007] Moreover, enabling the re-manifestation of a more perfect anisotropy is indicated by giving high shearing stress to the reference "orientation control of the Bi-Te system material by the strong shear addition knockout" (the 51st plastic-working union lecture meeting, 3-November 5, 2000) by **** and others at thermoelectric material using the dice which has a L character type path.
[0008] Drawing 16 is drawing which explains typically the method currently indicated by the above-mentioned reference, and, in (A) of drawing 16 , (B) shows the state after punch press before punch press. In this method, the Bi-Te system material 220 is enclosed into the dice 221 which has the L character type path which consists of an entrance-side path 225 and an outlet side path 227, and it presses by punch 223. Material 220 is extruded receiving strong shearing stress in the right-angled section X of a path. At this time, a skid occurs in the easy sliding surface (cleavage plane) of a Bi-Te crystal, and the rearrangement of the crystal is carried out by causing rotation simultaneously.
[0009]
[Problem(s) to be Solved by the Invention] However, in recent years, development of a thermoelement with a more high performance is progressing with highly-efficient-izing and improvement in the speed of optoelectronics, semiconductor laser, etc. to which a thermoelement is applied. Furthermore, thermoelectrical efficiency-of-element-mass production method is also demanded by development of this field.
[0010] Although according to the method currently indicated by above-mentioned JP,2000-124512,A sufficient shearing stress is obtained near the contact surface of the material in a dice, and a dice and it is easy to carry out the rearrangement of

the crystal, obtaining the still more uniform amount of preferred orientation is expected by abolishing the difference of the shearing stress of the core C of the material shown in drawing 15 (B), and Flank P.
[0011] Moreover, according to the method currently indicated by "orientation control of the Bi-Te system material by the strong shear addition knockout", even if material takes which portion in a cross section, in order that it may receive shearing stress uniformly, a product with a uniform property is obtained in the interior of material. However, it is only 1 time at the time of passing the right-angled section (L character type section) X of a dice that material receives shearing stress. For this reason, the amount of the shearing stress added cannot say that it is enough, but sufficient orientation is hard to be acquired.
[0012] Multiple-times addition of the shearing stress can be carried out by making the configuration of the entrance of a dice, and an outlet the same, and on the other hand, carrying out L character extrusion of multiple times in the L character extrusion of other conventional metallic materials. However, when using weak brittle materials, such as Bi-Te, it is necessary to add compressive stress at an outlet by making an outlet smaller than an entrance. This is for material to break in the L character section (buckling), when the configuration of an entrance and an outlet is made equal. Therefore, in fabrication of thermoelectric material, L character extrusion of multiple times cannot be performed and multiple-times addition of the shearing stress cannot be carried out.
[0013] Then, in view of the above-mentioned point, this invention aims at offering the extruding equipment and the extruding method of manufacturing thermoelectric material with a high thermoelectrical performance by adding sufficient shearing stress for material.
[0014]
[Means for Solving the Problem] In order to solve the above technical problem, the extruding equipment concerning the 1st viewpoint of this invention It is the 2nd extrusion path continued for the 1st extrusion path located in the entrance side of material, and the 1st extrusion path. The 2nd extrusion path which accomplishes a larger angle smaller than 180 degrees than 0 times to the 1st extrusion path is formed at least, and the dice which has the field where the cross section decreases toward the outlet side of material is provided in one of extrusion paths.
[0015] Shearing stress can be added also in this portion by extruding L characters, and being alike, in addition extracting one of extrusion paths, and considering as a configuration. Therefore, since the shearing stress in the case of [each] extrusion usually can be applied with L character extrusion, crystal grain turns minutely further and the amount of preferred orientation improves. Although the outlet configuration was made small and destruction (buckling) of material was prevented in the conventional L character extrusion, according to the 1st viewpoint of this invention, destruction (buckling) of material can be prevented by extracting the last extrusion path like the usual extrusion type, and considering as a configuration.
[0016] Moreover, the extruding equipment concerning the 2nd viewpoint of this invention It is the 2nd extrusion path continued for the 1st extrusion path located in the entrance side of material, and the 1st extrusion path. The dice with which the 2nd extrusion path which accomplishes a larger angle smaller than 180 degrees than 0 times to the 1st extrusion path was formed at least, The extrusion tool for pushing the material poured into the 1st extrusion path and the presser-foot tool for pushing back the material extruded from the 2nd extrusion path are provided.
[0017] According to the 2nd viewpoint of this invention, destruction (buckling) of material can be prevented by having the tool which pushes back the material extruded from the 2nd extrusion path of a dice. Moreover, since high compressive stress can be added from the 2nd extrusion path, the shearing stress in the L character section also becomes high. Then, repeat extrusion can also be performed by pressing down with extrusion punch 13, reversing the movement of punch 14, and making it go. Furthermore, since the configuration of the 1st extrusion path and the 2nd extrusion path can be made the same, the repeat extrusion of material becomes possible. Therefore, using the same equipment, by carrying out multiple-times addition of the shearing stress, crystal grain turns minutely further and the amount of preferred orientation improves.
[0018] It is desirable for each of the 1st and 2nd extrusion paths to have a rectangle cross section above. By making a cross section into a rectangle, the variation in the shearing stress in the cross direction of a dice can be abolished, and shearing stress can be equalized. Moreover, if it is made for a dice to have two or more outlets, since two or more material can be manufactured at a time, it is suitable for mass production.
[0019] Moreover, the extruding equipment concerning the 3rd viewpoint of this invention The 1st extrusion path located in the entrance side of the material prepared in the 1st direction, The 2nd extrusion path located in the entrance side of the material prepared in the 2nd direction, It is the 3rd extrusion path continued for the 1st and 2nd extrusion paths, and the dice with which the 3rd extrusion path which accomplishes a larger angle smaller than 180 degrees than 0 times to the 1st and 2nd extrusion paths was formed at least is provided.
[0020] Since it extrudes for the 3rd path according to the 3rd viewpoint of this invention, pushing on thermoelectric material from both sides in the 1st and 2nd paths, and putting a pressure, the shearing stress of a bilateral symmetry is added to thermoelectric material. Therefore, the symmetric property of the orientation of crystal grain can be raised in thermoelectric material.
[0021] The extruding method concerning this invention performs extruding of material using one of above extruding equipments. When using the extruding equipment especially applied to the 1st viewpoint of this invention, it is possible by performing extruding of material two or more times to make crystal grain detailed further, making the cross section of material small for every one processing.
[0022] Moreover, when using the extruding equipment concerning the 1st of this invention, and the 2nd viewpoint, it is desirable to perform extruding of material two or more times, putting in dummy material at the nose of cam of material. In case multiple-times extrusion of L characters is performed especially, destruction (buckling) of material can be prevented. Furthermore, it is desirable to perform extruding of material above between heat. In this case, it is hard coming to destroy material and recrystallization becomes easy to happen.
[0023]
[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained based on a drawing. In addition, the reference number same about the same component is attached, and explanation is omitted. Drawing 1 is drawing showing the outline of the extruding equipment concerning the 1st operation gestalt of this invention. As shown in drawing 1 , extruding equipment 10 contains the dice 11 which are the punch (extrusion tool) 13 which extrudes the

thermoelectric material 20 by which powder molding was carried out, and the metal mold which makes the thermoelectric material 20 extruded by punch 13 deform plastically. Punch 13 moves up and down with the slide 1 driven with an actuator (oil hydraulic cylinder). The extrusion pressure of punch 13 is measured by the load cell 2, and the variation rate of punch 13 is measured by the displacement gage 5. By acting as the monitor of the relation between the measurement value of a displacement gage 5, and elapsed time, the drive of slide 1 is controllable so that punch 13 extrudes thermoelectric material 20 at an almost fixed extrusion speed.

[0024] On the base 7 in which the dice 11 is installed, the heater 6 for heating a dice 11 and thermoelectric material 20 is installed. By using a heater 6, it is possible to perform hot-extrusion processing. The temperature of a dice 11 is measured by the temperature sensor 8 arranged near the dice 11. By feeding back the measurement value of a temperature sensor 8 and controlling the calorific value of a heater 6, a dice 11 and thermoelectric material 20 can be maintained at desired temperature.

[0025] As for hot-extrusion processing, it is desirable in inert gas atmosphere, such as an argon, or a vacuum to perform extrusion speed as for example, 0.1 mm/min, keeping more desirable 350 degrees C - 600 degrees C of working temperatures at 420 degrees C - about 500 degrees C. In addition, in this operation form, although the dice 11 was fixed and punch 13 was moved, punch 13 may be fixed to this reverse and a dice 11 may be moved to it.

[0026] Drawing 2 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 1st operation form of this invention, and punch, and (A) of drawing 2 and (B) show two states under extruding. The entrance-side path 15 in which punch 13 is taken in and out of a dice 11 up and down, and the outlet side path 17 by which mold goods are extruded are formed. The entrance-side path 15 and the outlet side path 17 are open for free passage (continuation), and the shaft of the longitudinal direction of the entrance-side path 15 and the shaft of the longitudinal direction of the outlet side path 17 form the angle theta. In this invention, it is required for an angle theta to be in the larger range smaller than 180 degrees than 0 degree, and it may be 45-135 degrees desirably. The angle theta is made into about 90 degrees in the following operation forms.

[0027] The entrance-side path 15 has a square (preferably rectangle) cross-section configuration, and the cross section is simultaneously regularity in the longitudinal direction of a path. The outlet side path 17 is formed so that it may have a square (preferably rectangle) cross-section configuration and may have the field where the cross section decreases toward the outlet of a dice 11. That is, the outlet side path 17 contains free passage section 17a with the entrance-side path 15, converging section 17b to which the cross section decreases gradually, and that the cross section's has decreased diameter reduction section 17c. In addition, as for the cross section of the outlet side path 17, it is desirable to set almost constant a crosswise (direction perpendicular to space) size, and to apply drawing only in the vertical direction in drawing.

[0028] As a thermoelectric material used for manufacture of a thermoelement, compounds containing these, such as antimony, a bismuth, a selenium, a tellurium, cobalt, manganese, silicon, zinc, magnesium, iron, and germanium, are mentioned. Extruding is performed to the ingot material, the fine particles, the green compact, the sintered compacts, and these processing objects of such a material.

[0029] If it explains in more detail, a selenium (Se) and a tellurium (Te) will be used as a VI group element, for example, using antimony (Sb) and a bismuth (Bi) as a V group element. The solid solution of V group element and VI group element has hexagonal structure. About concrete composition of thermoelectric material, the dopant of P type can be added and used for the mixed-crystal system solid solution of a bismuth telluride (Bi2Te3) and tellurium-ized antimony (Sb2Te3) as a material of a P type element, or the dopant of N type can be added and used for the mixed-crystal system solid solution of a bismuth telluride (Bi2Te3) and a selenium-ized bismuth (Bi2Se3) as a material of an N type element.

[0030] If thermoelectric material 20 is poured into the entrance-side path 15 and punch 13 is dropped in case thermoelectric material 20 carries out extruding using a dice 11, mold goods will be extruded from the outlet side path 17. At this time, as shown in drawing 2 (B), various shearing stress is added to a sintered compact 20. The boundary section X which the entrance-side path 15 and the outlet side path 17 open for free passage at a right angle mostly serves as a shear zone, and thermoelectric material 20 receives strong shearing stress in the boundary section X.

[0031] Furthermore, if thermoelectric material 20 progresses to the outlet side path 17, external force will be received [of converging section 17b of this trajectory / E] from the side, and thermoelectric material 20 will deform plastically. Therefore, since the shearing stress in the case of [each] extrusion usually can be applied with L character extrusion, crystal grain turns minutely further and the amount of preferred orientation improves. By making the cross section of a trajectory into a rectangle especially, the variation in the shearing stress in the cross direction of a dice can be abolished, and shearing stress can be equalized. Moreover, since the configuration of the outlet side of a dice 11 is a drawing configuration as mentioned above, it can restrain the material which comes out in response to processing from the outlet of a dice 11, and can prevent destruction (buckling) of material.

[0032] Next, the 2nd operation form of this invention is explained. Drawing 3 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 2nd operation form of this invention, and punch, and, in (A) of drawing 3 , (B) shows the state after punch press before punch press.

[0033] The extruding equipment concerning this operation form is equipped with two punch 13 and 14. The entrance-side path 25 in which punch 13 is taken in and out of a dice 21 up and down, and the outlet side path 27 in which punch 14 is taken in and out of right and left are formed. In a dice 21, the entrance-side path 25 and the outlet side path 27 are open for free passage. The entrance-side path 25 and the outlet side path 27 have the cross-section configuration of the same square (preferably rectangle), and it is [the cross section of each path] desirable in a longitudinal direction that it is simultaneously regularity. The extrusion punch (extrusion tool) 13 for pushing on the entrance-side path 25 the material poured into this trajectory is formed so that this path may be slid. Moreover, the presser-foot punch (presser-foot tool) 14 which applies back pressure to the outlet side path 27 by pushing back the material extruded from this trajectory is formed so that this path may be slid.

[0034] In case thermoelectric material carries out extruding using a dice 21, while pouring thermoelectric material into the entrance-side path 25 and dropping extrusion punch 13, presser-foot punch 14 is retreated applying back pressure. At this time, as shown in drawing 3 (B), various shearing stress is added to thermoelectric material 20. That is, like the 1st operation form, the boundary section X which the entrance-side path 25 and the outlet side path 27 open for free passage at a right

angle mostly serves as a shear zone, and thermoelectric material 20 receives strong shearing stress in the boundary section X. Furthermore, since thermoelectric material 20 was pressed down in the outlet side path 27 and has received the high compressive stress S from punch 14, the shearing stress in the boundary section X becomes strong. Then, repeat extrusion can also be performed by pressing down with extrusion punch 13, reversing the movement of punch 14, and making it go.
[0035] Moreover, in this operation gestalt, the repeat extrusion of material becomes possible by making the same the cross-section configuration of the entrance-side path 25 and the outlet side path 27. In this case, since multiple-times shearing stress can be added to material, crystal grain turns minutely further and the amount of preferred orientation improves.
[0036] Next, the 3rd operation gestalt of this invention is explained. Drawing 4 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 3rd operation gestalt of this invention, and punch, and (A) of drawing 4 and (B) show two states under extruding.
[0037] The extruding equipment concerning this operation form changes the configuration of two punch in the 2nd operation form. Extrusion punch 23 slides the entrance-side path 25, while the extrusion side maintains parallel mostly with the cross section in the boundary section X of a dice 21 which is not carried thermoelectric-material 20. Moreover, presser-foot punch 24 slides the outlet side path 27, maintaining parallel mostly with the cross section in the boundary section X of a dice 21 which is not carried thermoelectric-material 20. Thereby, the direction of the extrusion force is made in agreement with the move direction of material, and more smooth extruding can be performed.
[0038] In addition, in this operation form, it is desirable to perform extruding, as the thermoelectric material 20 for extruding is created and the cleavage plane of a crystal becomes almost parallel to the shear side in the boundary section X of a dice 21 by starting bulk of the sintered thermoelectric material aslant.
[0039] Next, the 4th operation form of this invention is explained. Drawing 5 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 4th operation form of this invention, and punch. The entrance-side path 35 in which punch 33 is taken in and out of a dice 31 up and down, and the outlet side path 37 by which mold goods are extruded are formed. In a dice 31, the entrance-side path 35 and the outlet side path 37 are open for free passage.
[0040] The entrance-side path 35 is formed so that it may have a square (preferably rectangle) cross-section configuration and may have the field where the cross section decreases toward the free passage section with the outlet side path 37. That is, the entrance-side path 35 contains entrance section 35a of simultaneously regularity of the cross section, converging section 35b to which the cross section decreases gradually, and that the cross section's has decreased diameter reduction section 35c. The outlet side path 37 has a square (preferably rectangle) cross-section configuration, and the cross section is simultaneously regularity in the longitudinal direction of a path. In addition, as for the cross section of the entrance-side path 35, it is desirable to set almost constant a crosswise (direction perpendicular to space) size, and to apply drawing only in the vertical direction in drawing.
[0041] If thermoelectric material 20 is poured into the entrance-side path 35 and punch 33 is dropped in case thermoelectric material carries out extruding using a dice 31, mold goods will be extruded from the outlet side path 37. At this time, external force is received [of converging section 35b of the entrance-side path 35] from the side, and thermoelectric material 20 deforms plastically. Furthermore, if thermoelectric material 20 progresses to the outlet side path 37, the boundary section X which the entrance-side path 35 and the outlet side path 37 open for free passage at a right angle mostly will serve as a shear zone, and thermoelectric material 20 will receive strong shearing stress in the boundary section X. Therefore, since the shearing stress in the case of [each] extrusion and L character extrusion can usually be applied, crystal grain turns minutely further and the amount of preferred orientation improves. By making a cross section into a rectangle especially, the variation in the shearing stress in the cross direction of a dice can be abolished, and shearing stress can be equalized.
[0042] Next, the 5th operation gestalt of this invention is explained. Drawing 6 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 5th operation gestalt of this invention, and punch. The entrance-side path 45 in which punch 33 is taken in and out of a dice 41 up and down, and the outlet side path 47 by which mold goods are extruded are formed. In a dice 41, the entrance-side path 45 and the outlet side path 47 are open for free passage.
[0043] The entrance-side path 45 is formed so that it may have a square (preferably rectangle) cross-section configuration and may have the field where the cross section decreases toward the free passage section with the outlet side path 47. that is, the entrance-side path 45 contains converging section 45b to which entrance section 45a of about 1 law and the cross section decrease [the cross section] gradually The outlet side path 47 is formed so that it may have a square (preferably rectangle) cross-section configuration and may have the field where the cross section decreases toward the outlet of a dice 41. That is, the outlet side path 47 contains free passage section 47a with the entrance-side path 45, converging section 47b to which the cross section decreases gradually, and that the cross section's has decreased diameter reduction section 47c. In addition, as for the cross section of the entrance-side path 45 and the outlet side path 47, it is desirable to set almost constant a crosswise (direction perpendicular to space) size, and to apply drawing only in the vertical direction in drawing.
[0044] If thermoelectric material 20 is poured into the entrance-side path 45 and punch 33 is dropped in case thermoelectric material carries out extruding using a dice 41, mold goods will be extruded from the outlet side path 47. At this time, external force is received [of converging section 45b of the entrance-side path 45] from the side, and thermoelectric material 20 deforms plastically. Furthermore, if thermoelectric material 20 progresses to the outlet side path 47, the boundary section X which the entrance-side path 45 and the outlet side path 47 open for free passage at a right angle mostly will serve as a shear zone, and thermoelectric material 20 will receive strong shearing stress. In addition, external force is received [of converging section 47b of the outlet side path 47] from the side, and thermoelectric material 20 deforms plastically.
[0045] Therefore, since the shearing stress in the case of [each] L character extrusion and the usual extrusion of two batches can be applied, crystal grain turns minutely further and the amount of preferred orientation improves. By making a cross section into a rectangle especially, the variation in the shearing stress in the cross direction of a dice can be abolished, and shearing stress can be equalized. Moreover, since the configuration of the outlet side of a dice 41 is a drawing configuration as mentioned above, it can restrain the material which comes out in response to processing from the outlet of a dice 41, and can prevent destruction (buckling) of material.
[0046] Next, the 6th operation gestalt of this invention is explained. Drawing 7 is the side cross section showing the structure

of the dice used in the extruding equipment concerning the 6th operation gestalt of this invention, and punch. The entrance-side path 55 in which punch 13 is taken in and out of the dice 51 of the extruding equipment concerning this operation gestalt up and down, and two outlet side paths 57 and 58 in which mold goods are extruded are formed. The entrance-side path 55 and the outlet side paths 57 and 58 are open for free passage, and the outlet side paths 57 and 58 accomplished the angle of about 90 degrees to the entrance-side path 55, respectively, and are mutually prolonged in opposite direction. Moreover, like the 1st operation gestalt, the outlet side paths 57 and 58 are formed so that the cross section may decrease toward the outlet of a dice.

[0047] If thermoelectric material 20 is poured into the entrance-side path 55 and punch 13 is dropped, mold goods will be extruded from two outlet side paths 57 and 58. At this time, the two boundary sections X and Y which the entrance-side path 55 and two outlet side paths 57 and 58 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20.

[0048] In addition, although two outlet side paths 57 and 58 were established in this operation form so that the angle of about 90 degrees might be accomplished to the entrance-side path 55, respectively, you may establish three or more outlet side paths. Moreover, the angle of an entrance-side path and an outlet side path to accomplish has [that what is necessary is just to be in the larger range smaller than 180 degrees than 0 degree] the especially desirable range of 45 degrees - 135 degrees.

[0049] Next, the 7th operation form of this invention is explained. Drawing 8 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 7th operation form of this invention, and punch. The extruding equipment concerning this operation form is equipped with three punch 12, 13, and 14. The entrance-side path 65 in which punch 13 is taken in and out of a dice 61 up and down, the outlet side path 67 in which punch 12 is taken in and out of right and left, and the outlet side path 68 in which punch 14 is taken in and out of right and left are formed. In a dice 61, the entrance-side path 65 and the outlet side paths 67 and 68 are open for free passage. The extrusion punch (extrusion tool) 13 for pushing on the entrance-side path 65 the material poured into this trajectory is formed so that this path may be slid. Moreover, the presser-foot punch (presser-foot tool) 12 which applies back pressure to the outlet side path 67 by pushing back the material extruded from this trajectory is formed so that this path may be slid. Similarly, by pushing back the material extruded from this trajectory, the presser-foot punch 14 to which back pressure is applied is formed in the outlet side path 68 so that this path may be slid.

[0050] In case thermoelectric material carries out extruding using a dice 61, while pouring thermoelectric material into the entrance-side path 65 and dropping extrusion punch 13, presser-foot punch 12 and 14 is retreated applying back pressure. At this time, the two boundary sections X and Y which the entrance-side path 65 and two outlet side paths 67 and 68 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20. Furthermore, since thermoelectric material 20 was pressed down in the outlet side paths 67 and 68 and has received high compressive stress from punch 12 and 14, the shearing stress in the boundary sections X and Y becomes strong.

[0051] Next, the 8th operation form of this invention is explained. Drawing 9 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 8th operation form of this invention, and punch. The middle path 76 which connects to the dice 71 of the extruding equipment concerning this operation form the entrance-side path 75 punch 13 is taken in and out of which up and down, the outlet side path 77 by which mold goods are extruded, and the entrance-side path 75 and the outlet side path 77 is formed. The angle which each path is opening for free passage and the entrance-side path 75 and the middle path 76 make is about 90 degrees, and the angle which the middle path 76 and the outlet side path 77 make is about 90 degrees. The cross-section configuration of each path is a square (preferably rectangle). Moreover, the cross section of the entrance-side path 75 and the cross section of the middle path 76 are equal. The outlet side path 77 is formed so that the cross section may decrease toward the outlet of a dice 71. That is, the outlet side path 77 contains converging section 77a to which the cross section decreases gradually from the free passage section with the middle path 76, and that the cross section's has decreased diameter reduction section 77b.

[0052] If thermoelectric material is poured into the entrance-side path 75 and punch 13 is dropped, a sintered compact will be extruded from the outlet side path 77 through the middle path 76. At this time, a shear zone strong against thermoelectric material 20 is added in a path open for free passage in two places, the boundary section X which the entrance-side path 75 and the middle path 76 open for free passage right-angled, and the boundary section Y which the middle path 76 and the outlet side path 77 open for free passage right-angled. Furthermore, since converging section 77a is formed in the outlet side path 77, also in this converging section 77a, external force is received [E] from the side, and thermoelectric material 20 deforms plastically. Therefore, it is possible to make crystal grain turn minutely further and to raise a stacking tendency. Moreover, since the configuration of the outlet side of a dice 71 is a drawing configuration as mentioned above, it can restrain the material which comes out in response to processing from the outlet of a dice 71, and can prevent destruction (buckling) of material.

[0053] Next, the 9th operation form of this invention is explained. Drawing 10 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 9th operation form of this invention, and punch. The middle path 86 which connects to the dice 81 of the extruding equipment concerning this operation form the entrance-side path 85 punch 13 is taken in and out of which up and down, the outlet side path 87 by which mold goods are extruded, and the entrance-side path 85 and the outlet side path 87 is formed. The angle which each path is opening for free passage and the entrance-side path 85 and the middle path 86 make is about 90 degrees, and the angle which the middle path 86 and the outlet side path 87 make is about 90 degrees. The cross-section configuration of each path is a square (preferably rectangle). Moreover, the cross section of each path is small in order of the entrance-side path 85, the middle path 86, and the outlet side path 87. Furthermore, the outlet side path 87 is formed so that the cross section may decrease toward the outlet of a dice 81.

[0054] If thermoelectric material 20 is poured into the entrance-side path 85 and punch 13 is dropped, a sintered compact will be extruded from the outlet path 87 through the middle path 86. Since the cross section is decreasing as these paths go to the outlet side of material at this time, it is very effective for preventing buckling of material.

[0055] When an extrusion path has two or more bends as in the 8th operation form or the 9th operation form especially, destruction of material can be suppressed by putting in dummy material at the nose of cam of thermoelectric material 20, and performing extruding.

[0056] Next, the 10th operation form of this invention is explained. In the following operation forms, T character extrusion is

performed using two punch. Drawing 11 is drawing showing the outline of the extruding equipment concerning the 10th operation form of this invention. As shown in drawing 11 , extruding equipment 100 contains two punch 112 and 113 which extrudes the thermoelectric material 20 by which powder molding was carried out, and the dice 111 which is the metal mold which makes the thermoelectric material 20 extruded by punch 112 and 113 deform plastically. Punch 112 and 113 moves to right and left with the slides 101 and 102 driven with an actuator (oil hydraulic cylinder). The extrusion pressure of punch 112 and 113 is measured by load cells 103 and 104, respectively, and the variation rate of punch 112 and 113 is measured by displacement gages 105 and 106, respectively. By acting as the monitor of the relation between the measurement value of displacement gages 105 and 106, and elapsed time, the drive of slides 101 and 102 is controllable so that punch 112 and 113 extrudes thermoelectric material 20 at an almost fixed extrusion speed.

[0057] On the base 107 in which the dice 111 is installed, the heater 108 for heating a dice 111 and thermoelectric material 20 is installed. By using a heater 108, it is possible to perform hot-extrusion processing. The temperature of a dice 111 is measured by the temperature sensor 109 arranged near the dice 111. By feeding back the measurement value of a temperature sensor 109 and controlling the calorific value of a heater 108, a dice 111 and thermoelectric material 20 can be maintained at desired temperature.

[0058] As for hot-extrusion processing, it is desirable in inert gas atmosphere, such as an argon, or a vacuum to perform extrusion speed as for example, 0.1 mm/min, keeping more desirable 350 degrees C - 600 degrees C of working temperatures at 420 degrees C - about 500 degrees C.

[0059] Drawing 12 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 10th operation form of this invention, and punch. Two entrance-side paths 121 and 122 in which two punch 112 and 113 is taken in and out of right and left, respectively, and the outlet side path 123 by which mold goods are extruded are formed in the dice 111 of the extruding equipment concerning this operation form. The entrance-side paths 112 and 113 and the outlet side path 123 are open for free passage. In this invention, it is required for the outlet side path 123 to accomplish a larger angle smaller than 180 degrees than 0 degree to the entrance-side paths 112 and 113, and it may be 45 degrees - 135 degrees desirably. In the following operation forms, the angle which makes this angle about 90 degrees, and the entrance-side paths 112 and 113 constitute is made into about 180 degrees.

[0060] If thermoelectric material 20 is poured in from the entrance-side path 121 or 122 and punch 112 and 113 is driven, thermoelectric material 20 will be equally pressurized from both sides, and mold goods will be extruded from the outlet side path 123. At this time, the two boundary sections X and Y which two entrance-side paths 121 and 122 and outlet side paths 123 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20. Thus, the orientation of the crystal grain in thermoelectric material serves as a bilateral symmetry to the longitudinal plane of symmetry of thermoelectric material by adding shearing stress equally from right and left.

[0061] Next, the 11th operation form of this invention is explained. Drawing 13 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 11th operation form of this invention, and punch. The entrance-side paths 131 and 132 in which two punch 112 and 113 is taken in and out of right and left, respectively, and two outlet side paths 133 in which mold goods are extruded are formed in the dice 130 of the extruding equipment concerning this operation form. Like the 1st operation form, the converging section 134 is formed in the outlet side path 133 so that the cross section may decrease toward the outlet of a dice.

[0062] If thermoelectric material 20 is poured into the entrance-side path 131 or 132 and punch 112 and 113 is driven, thermoelectric material 20 will be equally pressurized from both sides, and mold goods will be extruded from the outlet side path 133. At this time, the two boundary sections X and Y which two entrance-side paths 131 and 132 and outlet side paths 133 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20. Furthermore, if thermoelectric material 20 progresses to the outlet side path 133, external force will be received of the converging section 134 of this trajectory / E] from the side, and thermoelectric material 20 will deform plastically. The crystal grain which constitutes thermoelectric material turns minutely further by this, and the amount of preferred orientation improves.

[0063] According to this operation form, both extrusion usually receives symmetrical shearing stress to the center line of thermoelectric material with T character extrusion. Therefore, over the whole interior of thermoelectric material, the orientation of a grain boundary is a bilateral symmetry and the thermoelectric material which does not have variation in the property of the organization by the position can be manufactured.

[0064] Next, the 12th operation form of this invention is explained. Drawing 14 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 12th operation form of this invention, and punch. The extruding equipment concerning this operation form is equipped with three punch 112, 113, and 114. The entrance-side paths 141 and 142 in which two punch 112 and 113 is taken in and out of right and left, respectively, and the outlet side path 143 punch 114 is taken in and out of which up and down are formed in the dice 140. The extrusion punch 112 and 113 for pushing on the entrance-side paths 141 and 142 the material poured into this trajectory from both sides is formed so that this path may be slid. Moreover, the presser-foot punch (presser-foot tool) 114 which applies back pressure to the outlet side path 67 by pushing back the material extruded from this trajectory is formed so that this path may be slid.

[0065] In case thermoelectric material carries out extruding using a dice 140, while pouring in thermoelectric material from the entrance-side path 141 or 142 and making extrusion punch 112 and 113 drive, presser-foot punch 114 is retreated applying back pressure. At this time, the two boundary sections X and Y which two entrance-side paths 141 and 142 and outlet side paths 143 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20. Furthermore, since thermoelectric material 20 was pressed down in the outlet side path 143 and has received high compressive stress from punch 114, the shearing stress in the boundary sections X and Y becomes strong.

[0066]

[Effect of the Invention] Like, according to this invention, since the shearing stress in the case of [each] extrusion usually described above can be applied with L character extrusion, crystal grain can be turned further minutely and the amount of preferred orientation can be raised. Thermal conductivity kappa becomes small by detailed-ization of this crystal grain, and a performance index Z improves. Moreover, a performance index Z improves also by improvement in the amount of preferred orientation. Therefore, it becomes possible to manufacture thermoelectric material with a high thermoelectrical performance.

Moreover, in applying shearing stress by T character extrusion, while making crystal grain detailed, it has a symmetrical stacking tendency to the direction of extrusion, and it becomes possible to manufacture a homogeneous thermoelectric material which does not have variation in the property of the organization by the position.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the extruding equipment suitable for extruding of the thermoelectric material used in order to manufacture a thermoelement especially, and the extruding method about the extruding equipment and the extruding method which are used in order to perform extruding which is a kind of plastic deformation processing to a metal, a semiconductor material, an oxide, etc. generally.

[Translation done.]

PRIOR ART

[Description of the Prior Art] A thermoelement means the element using the thermoelectric effects, such as the Thomson effect, a Peltier effect, and the Seebeck effect, a thermocouple, an electronic cooling element, etc., and far-reaching use attracts attention from a property that handling is simply [structure] easy and stable being maintainable. Especially as an electronic cooling element, since the precise temperature control a local hypothermia and near a room temperature is possible, research and development are widely furthered towards the application to temperature control, such as optoelectronics and semiconductor laser, a small refrigerator, etc.

[0003] A big thing of the performance index Z expressed with 2/[of Z=alpha] rhokappa is desired using specific resistance (resistivity) rho, thermal conductivity kappa, and Seebeck-coefficient alpha as a thermoelement. Moreover, many of thermoelectrical semiconductor materials have an anisotropy resulting from the crystal structure. Generally, an anisotropy crystal has cleavage and its material strength is brittle. For this reason, as a charge of real material, not single crystal material but the polycrystal material which carried out orientation to the big crystal orientation of a performance index is used. In order to obtain a good performance index, it is effective to establish the process of plastic working, such as extruding which sinters the crystal material made to solidify after fine-particles-izing, and gives shearing stress after sintering.

[0004] While raising the amount of preferred orientation of a thermoelectrical semiconductor material to the Japan patent application public presentation (provisional publication of a patent) No. 124512 [2000 to] official report, the rate of the yield at the time of starting a rectangular parallelepiped-like thermoelement is raised, and the manufacture method of the thermoelectrical semiconductor material which makes a surface-lapping process and a consolidation process possible is indicated.

[0005] Drawing 15 is drawing which explains typically the manufacture method of the thermoelectrical semiconductor material currently indicated by JP,2000-124512,A, and, in (A) of drawing 15 , (B) shows the state after punch press before punch press. In this manufacture method, thermoelectric material is used as the rectangular parallelepiped-like sintered compact 210, this sintered compact 210 is poured into a dice 211, and punch 213 is dropped. The entrance-side path 215 into which a sintered compact 210 is poured, and the extrusion path 217 of the shape of a rectangular parallelepiped with the cross section smaller than the entrance-side path 215 are formed in the dice 211. A sintered compact 210 is extruded from the extrusion path 217 by the press force of punch 213 down [D], and rectangular parallelepiped-like mold goods are obtained according to it. In the case of this extrusion, a sintered compact 210 deforms [of a dice 211 / E] plastically in response to external force from the side. For this reason, the external force concerning material is large, and tends to require the force for the whole material.

[0006] Therefore, according to this manufacture method, dynamic recrystallization under destruction by plastic deformation and fabrication is performed good, and crystal grain makes it detailed. Thermal conductivity kappa becomes small by detailed-ization of this crystal grain, and a performance index Z improves. Moreover, rather than hot forging, external force is added, a degree is good, an anisotropy increases and a performance index improves.

[0007] Moreover, enabling the re-manifestation of a more perfect anisotropy is indicated by giving high shearing stress to the reference "orientation control of the Bi-Te system material by the strong shear addition knockout" (the 51st plastic-working union lecture meeting, 3-November 5, 2000) by **** and others at thermoelectric material using the dice which has a L character type path.

[0008] Drawing 16 is drawing which explains typically the method currently indicated by the above-mentioned reference, and, in (A) of drawing 16 , (B) shows the state after punch press before punch press. In this method, the Bi-Te system material 220 is enclosed into the dice 221 which has the L character type path which consists of an entrance-side path 225 and an outlet side path 227, and it presses by punch 223. Material 220 is extruded receiving strong shearing stress in the right-angled section X of a path. At this time, a skid occurs in the easy sliding surface (cleavage plane) of a Bi-Te crystal, and the rearrangement of the crystal is carried out by causing rotation simultaneously.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] Like, according to this invention, since the shearing stress in the case of [each] extrusion usually described above can be applied with L character extrusion, crystal grain can be turned further minutely and the amount of preferred orientation can be raised. Thermal conductivity kappa becomes small by detailed-ization of this crystal grain, and a performance index Z improves. Moreover, a performance index Z improves also by improvement in the amount of preferred orientation. Therefore, it becomes possible to manufacture thermoelectric material with a high thermoelectrical performance. Moreover, in applying shearing stress by T character extrusion, while making crystal grain detailed, it has a symmetrical stacking tendency to the direction of extrusion, and it becomes possible to manufacture a homogeneous thermoelectric material which does not have variation in the property of the organization by the position.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in recent years, development of a thermoelement with a more high performance is progressing with highly-efficient-izing and improvement in the speed of optoelectronics, semiconductor laser, etc. to which a thermoelement is applied. Furthermore, thermoelectrical efficiency-of-element-mass production method is also demanded by development of this field.
[0010] Although according to the method currently indicated by above-mentioned JP,2000-124512,A sufficient shearing stress is obtained near the contact surface of the material in a dice, and a dice and it is easy to carry out the rearrangement of the crystal, obtaining the still more uniform amount of preferred orientation is expected by abolishing the difference of the shearing stress of the core C of the material shown in drawing 15 (B), and Flank P.
[0011] Moreover, according to the method currently indicated by "orientation control of the Bi-Te system material by the strong shear addition knockout", even if material takes which portion in a cross section, in order that it may receive shearing stress uniformly, a product with a uniform property is obtained in the interior of material. However, it is only 1 time at the time of passing the right-angled section (L character type section) X of a dice that material receives shearing stress. For this reason, the amount of the shearing stress added cannot say that it is enough, but sufficient orientation is hard to be acquired.
[0012] Multiple-times addition of the shearing stress can be carried out by making the configuration of the entrance of a dice, and an outlet the same, and on the other hand, carrying out L character extrusion of multiple times in the L character extrusion of other conventional metallic materials. However, when using weak brittle materials, such as Bi-Te, it is necessary to add compressive stress at an outlet by making an outlet smaller than an entrance. This is for material to break in the L character section (buckling), when the configuration of an entrance and an outlet is made equal. Therefore, in fabrication of thermoelectric material, L character extrusion of multiple times cannot be performed and multiple-times addition of the shearing stress cannot be carried out.
[0013] Then, in view of the above-mentioned point, this invention aims at offering the extruding equipment and the extruding method of manufacturing thermoelectric material with a high thermoelectrical performance by adding sufficient shearing stress for material.

[Translation done.]

MEANS

[Means for Solving the Problem] In order to solve the above technical problem, the extruding equipment concerning the 1st viewpoint of this invention It is the 2nd extrusion path continued for the 1st extrusion path located in the entrance side of material, and the 1st extrusion path. The 2nd extrusion path which accomplishes a larger angle smaller than 180 degrees than 0 times to the 1st extrusion path is formed at least, and the dice which has the field where the cross section decreases toward the outlet side of material is provided in one of extrusion paths.

[0015] Shearing stress can be added also in this portion by extruding L characters, and being alike, in addition extracting one of extrusion paths, and considering as a configuration. Therefore, since the shearing stress in the case of [each] extrusion usually can be applied with L character extrusion, crystal grain turns minutely further and the amount of preferred orientation improves. Although the outlet configuration was made small and destruction (buckling) of material was prevented in the conventional L character extrusion, according to the 1st viewpoint of this invention, destruction (buckling) of material can be prevented by extracting the last extrusion path like the usual extrusion type, and considering as a configuration.

[0016] Moreover, the extruding equipment concerning the 2nd viewpoint of this invention It is the 2nd extrusion path continued for the 1st extrusion path located in the entrance side of material, and the 1st extrusion path. The dice with which the 2nd extrusion path which accomplishes a larger angle smaller than 180 degrees than 0 times to the 1st extrusion path was formed at least, The extrusion tool for pushing the material poured into the 1st extrusion path and the presser-foot tool for pushing back the material extruded from the 2nd extrusion path are provided.

[0017] According to the 2nd viewpoint of this invention, destruction (buckling) of material can be prevented by having the tool which pushes back the material extruded from the 2nd extrusion path of a dice. Moreover, since high compressive stress can be added from the 2nd extrusion path, the shearing stress in the L character section also becomes high. Then, repeat extrusion can also be performed by pressing down with extrusion punch 13, reversing the movement of punch 14, and making it go. Furthermore, since the configuration of the 1st extrusion path and the 2nd extrusion path can be made the same, the repeat extrusion of material becomes possible. Therefore, using the same equipment, by carrying out multiple-times addition of the shearing stress, crystal grain turns minutely further and the amount of preferred orientation improves.

[0018] It is desirable for each of the 1st and 2nd extrusion paths to have a rectangle cross section above. By making a cross section into a rectangle, the variation in the shearing stress in the cross direction of a dice can be abolished, and shearing stress can be equalized. Moreover, if it is made for a dice to have two or more outlets, since two or more material can be manufactured at a time, it is suitable for mass production.

[0019] Moreover, the extruding equipment concerning the 3rd viewpoint of this invention The 1st extrusion path located in the entrance side of the material prepared in the 1st direction, The 2nd extrusion path located in the entrance side of the material prepared in the 2nd direction, It is the 3rd extrusion path continued for the 1st and 2nd extrusion paths, and the dice with which the 3rd extrusion path which accomplishes a larger angle smaller than 180 degrees than 0 times to the 1st and 2nd extrusion paths was formed at least is provided.

[0020] Since it extrudes for the 3rd path according to the 3rd viewpoint of this invention, pushing on thermoelectric material from both sides in the 1st and 2nd paths, and putting a pressure, the shearing stress of a bilateral symmetry is added to thermoelectric material. Therefore, the symmetric property of the orientation of crystal grain can be raised in thermoelectric material.

[0021] The extruding method concerning this invention performs extruding of material using one of above extruding equipments. When using the extruding equipment especially applied to the 1st viewpoint of this invention, it is possible by performing extruding of material two or more times to make crystal grain detailed further, making the cross section of material small for every one processing.

[0022] Moreover, when using the extruding equipment concerning the 1st of this invention, and the 2nd viewpoint, it is desirable to perform extruding of material two or more times, putting in dummy material at the nose of cam of material. In case multiple-times extrusion of L characters is performed especially, destruction (buckling) of material can be prevented. Furthermore, it is desirable to perform extruding of material above between heat. In this case, it is hard coming to destroy material and recrystallization becomes easy to happen.

[0023]

[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained based on a drawing. In addition, the reference number same about the same component is attached, and explanation is omitted. Drawing 1 is drawing showing the outline of the extruding equipment concerning the 1st operation gestalt of this invention. As shown in drawing 1 , extruding equipment 10 contains the dice 11 which are the punch (extrusion tool) 13 which extrudes the thermoelectric material 20 by which powder molding was carried out, and the metal mold which makes the thermoelectric material 20 extruded by punch 13 deform plastically. Punch 13 moves up and down with the slide 1 driven with an actuator (oil hydraulic cylinder). The extrusion pressure of punch 13 is measured by the load cell 2, and the variation rate of punch 13 is measured by the displacement gage 5. By acting as the monitor of the relation between the measurement value of a displacement gage 5, and elapsed time, the drive of slide 1 is controllable so that punch 13 extrudes thermoelectric material

20 at an almost fixed extrusion speed.
[0024] On the base 7 in which the dice 11 is installed, the heater 6 for heating a dice 11 and thermoelectric material 20 is installed. By using a heater 6, it is possible to perform hot-extrusion processing. The temperature of a dice 11 is measured by the temperature sensor 8 arranged near the dice 11. By feeding back the measurement value of a temperature sensor 8 and controlling the calorific value of a heater 6, a dice 11 and thermoelectric material 20 can be maintained at desired temperature.
[0025] As for hot-extrusion processing, it is desirable in inert gas atmosphere, such as an argon, or a vacuum to perform extrusion speed as for example, 0.1 mm/min, keeping more desirable 350 degrees C - 600 degrees C of working temperatures at 420 degrees C - about 500 degrees C. In addition, in this operation form, although the dice 11 was fixed and punch 13 was moved, punch 13 may be fixed to this reverse and a dice 11 may be moved to it.
[0026] Drawing 2 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 1st operation gestalt of this invention, and punch, and (A) of drawing 2 and (B) show two states under extruding. The entrance-side path 15 in which punch 13 is taken in and out of a dice 11 up and down, and the outlet side path 17 by which mold goods are extruded are formed. The entrance-side path 15 and the outlet side path 17 are open for free passage (continuation), and the shaft of the longitudinal direction of the entrance-side path 15 and the shaft of the longitudinal direction of the outlet side path 17 form the angle theta. In this invention, it is required for an angle theta to be in the larger range smaller than 180 degrees than 0 degree, and it may be 45-135 degrees desirably. The angle theta is made into about 90 degrees in the following operation gestalten.
[0027] The entrance-side path 15 has a square (preferably rectangle) cross-section configuration, and the cross section is simultaneously regularity in the longitudinal direction of a path. The outlet side path 17 is formed so that it may have a square (preferably rectangle) cross-section configuration and may have the field where the cross section decreases toward the outlet of a dice 11. That is, the outlet side path 17 contains free passage section 17a with the entrance-side path 15, converging section 17b to which the cross section decreases gradually, and that the cross section's has decreased diameter reduction section 17c. In addition, as for the cross section of the outlet side path 17, it is desirable to set almost constant a crosswise (direction perpendicular to space) size, and to apply drawing only in the vertical direction in drawing.
[0028] As a thermoelectric material used for manufacture of a thermoelement, compounds containing these, such as antimony, a bismuth, a selenium, a tellurium, cobalt, manganese, silicon, zinc, magnesium, iron, and germanium, are mentioned. Extruding is performed to the ingot material, the fine particles, the green compact, the sintered compacts, and these processing objects of such a material.
[0029] If it explains in more detail, a selenium (Se) and a tellurium (Te) will be used as a VI group element, for example, using antimony (Sb) and a bismuth (Bi) as a V group element. The solid solution of V group element and VI group element has hexagonal structure. About concrete composition of thermoelectric material, the dopant of P type can be added and used for the mixed-crystal system solid solution of a bismuth telluride (Bi2Te3) and tellurium-ized antimony (Sb2Te3) as a material of a P type element, or the dopant of N type can be added and used for the mixed-crystal system solid solution of a bismuth telluride (Bi2Te3) and a selenium-ized bismuth (Bi2Se3) as a material of an N type element.
[0030] If thermoelectric material 20 is poured into the entrance-side path 15 and punch 13 is dropped in case thermoelectric material 20 carries out extruding using a dice 11, mold goods will be extruded from the outlet side path 17. At this time, as shown in drawing 2 (B), various shearing stress is added to a sintered compact 20. The boundary section X which the entrance-side path 15 and the outlet side path 17 open for free passage at a right angle mostly serves as a shear zone, and thermoelectric material 20 receives strong shearing stress in the boundary section X.
[0031] Furthermore, if thermoelectric material 20 progresses to the outlet side path 17, external force will be received [of converging section 17b of this trajectory / E] from the side, and thermoelectric material 20 will deform plastically. Therefore, since the shearing stress in the case of [each] extrusion usually can be applied with L character extrusion, crystal grain turns minutely further and the amount of preferred orientation improves. By making the cross section of a trajectory into a rectangle especially, the variation in the shearing stress in the cross direction of a dice can be abolished, and shearing stress can be equalized. Moreover, since the configuration of the outlet side of a dice 11 is a drawing configuration as mentioned above, it can restrain the material which comes out in response to processing from the outlet of a dice 11, and can prevent destruction (buckling) of material.
[0032] Next, the 2nd operation gestalt of this invention is explained. Drawing 3 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 2nd operation gestalt of this invention, and punch, and, in (A) of drawing 3 , (B) shows the state after punch press before punch press.
[0033] The extruding equipment concerning this operation gestalt is equipped with two punch 13 and 14. The entrance-side path 25 in which punch 13 is taken in and out of a dice 21 up and down, and the outlet side path 27 in which punch 14 is taken in and out of right and left are formed. In a dice 21, the entrance-side path 25 and the outlet side path 27 are open for free passage. The entrance-side path 25 and the outlet side path 27 have the cross-section configuration of the same square (preferably rectangle), and it is [the cross section of each path] desirable in a longitudinal direction that it is simultaneously regularity. The extrusion punch (extrusion tool) 13 for pushing on the entrance-side path 25 the material poured into this trajectory is formed so that this path may be slid. Moreover, the presser-foot punch (presser-foot tool) 14 which applies back pressure to the outlet side path 27 by pushing back the material extruded from this trajectory is formed so that this path may be slid.
[0034] In case thermoelectric material carries out extruding using a dice 21, while pouring thermoelectric material into the entrance-side path 25 and dropping extrusion punch 13, presser-foot punch 14 is retreated applying back pressure. At this time, as shown in drawing 3 (B), various shearing stress is added to thermoelectric material 20. That is, like the 1st operation gestalt, the boundary section X which the entrance-side path 25 and the outlet side path 27 open for free passage at a right angle mostly serves as a shear zone, and thermoelectric material 20 receives strong shearing stress in the boundary section X. Furthermore, since thermoelectric material 20 was pressed down in the outlet side path 27 and has received the high compressive stress S from punch 14, the shearing stress in the boundary section X becomes strong. Then, repeat extrusion can also be performed by pressing down with extrusion punch 13, reversing the movement of punch 14, and making it go.
[0035] Moreover, in this operation form, the repeat extrusion of material becomes possible by making the same the

cross-section configuration of the entrance-side path 25 and the outlet side path 27. In this case, since multiple-times shearing stress can be added to material, crystal grain turns minutely further and the amount of preferred orientation improves.
[0036] Next, the 3rd operation form of this invention is explained. Drawing 4 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 3rd operation form of this invention, and punch, and (A) of drawing 4 and (B) show two states under extruding.
[0037] The extruding equipment concerning this operation gestalt changes the configuration of two punch in the 2nd operation gestalt. Extrusion punch 23 slides the entrance-side path 25, while the extrusion side maintains parallel mostly with the cross section in the boundary section X of a dice 21 which is not carried thermoelectric-material 20. Moreover, presser-foot punch 24 slides the outlet side path 27, maintaining parallel mostly with the cross section in the boundary section X of a dice 21 which is not carried thermoelectric-material 20. Thereby, the direction of the extrusion force is made in agreement with the move direction of material, and more smooth extruding can be performed.
[0038] In addition, in this operation gestalt, it is desirable to perform extruding, as the thermoelectric material 20 for extruding is created and the cleavage plane of a crystal becomes almost parallel to the shear side in the boundary section X of a dice 21 by starting bulk of the sintered thermoelectric material aslant.
[0039] Next, the 4th operation gestalt of this invention is explained. Drawing 5 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 4th operation gestalt of this invention, and punch. The entrance-side path 35 in which punch 33 is taken in and out of a dice 31 up and down, and the outlet side path 37 by which mold goods are extruded are formed. In a dice 31, the entrance-side path 35 and the outlet side path 37 are open for free passage.
[0040] The entrance-side path 35 is formed so that it may have a square (preferably rectangle) cross-section configuration and may have the field where the cross section decreases toward the free passage section with the outlet side path 37. that is, the entrance-side path 35 contains converging section 35b to which entrance section 35a of about 1 law and the cross section decrease [the cross section] gradually, and that the cross section's has decreased diameter reduction section 35c The outlet side path 37 has a square (preferably rectangle) cross-section configuration, and the cross section is simultaneously regularity in the longitudinal direction of a path. In addition, as for the cross section of the entrance-side path 35, it is desirable to set almost constant a crosswise (direction perpendicular to space) size, and to apply drawing only in the vertical direction in drawing.
[0041] If thermoelectric material 20 is poured into the entrance-side path 35 and punch 33 is dropped in case thermoelectric material carries out extruding using a dice 31, mold goods will be extruded from the outlet side path 37. At this time, external force is received [of converging section 35b of the entrance-side path 35] from the side, and thermoelectric material 20 deforms plastically. Furthermore, if thermoelectric material 20 progresses to the outlet side path 37, the boundary section X which the entrance-side path 35 and the outlet side path 37 open for free passage at a right angle mostly will serve as a shear zone, and thermoelectric material 20 will receive strong shearing stress in the boundary section X. Therefore, since the shearing stress in the case of [each] extrusion and L character extrusion can usually be applied, crystal grain turns minutely further and the amount of preferred orientation improves. By making a cross section into a rectangle especially, the variation in the shearing stress in the cross direction of a dice can be abolished, and shearing stress can be equalized.
[0042] Next, the 5th operation gestalt of this invention is explained. Drawing 6 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 5th operation gestalt of this invention, and punch. The entrance-side path 45 in which punch 33 is taken in and out of a dice 41 up and down, and the outlet side path 47 by which mold goods are extruded are formed. In a dice 41, the entrance-side path 45 and the outlet side path 47 are open for free passage.
[0043] The entrance-side path 45 is formed so that it may have a square (preferably rectangle) cross-section configuration and may have the field where the cross section decreases toward the free passage section with the outlet side path 47. that is, the entrance-side path 45 contains converging section 45b to which entrance section 45a of about 1 law and the cross section decrease [the cross section] gradually The outlet side path 47 is formed so that it may have a square (preferably rectangle) cross-section configuration and may have the field where the cross section decreases toward the outlet of a dice 41. That is, the outlet side path 47 contains free passage section 47a with the entrance-side path 45, converging section 47b to which the cross section decreases gradually, and that the cross section's has decreased diameter reduction section 47c. In addition, as for the cross section of the entrance-side path 45 and the outlet side path 47, it is desirable to set almost constant a crosswise (direction perpendicular to space) size, and to apply drawing only in the vertical direction in drawing.
[0044] If thermoelectric material 20 is poured into the entrance-side path 45 and punch 33 is dropped in case thermoelectric material carries out extruding using a dice 41, mold goods will be extruded from the outlet side path 47. At this time, external force is received [of converging section 45b of the entrance-side path 45] from the side, and thermoelectric material 20 deforms plastically. Furthermore, if thermoelectric material 20 progresses to the outlet side path 47, the boundary section X which the entrance-side path 45 and the outlet side path 47 open for free passage at a right angle mostly will serve as a shear zone, and thermoelectric material 20 will receive strong shearing stress. In addition, external force is received [of converging section 47b of the outlet side path 47] from the side, and thermoelectric material 20 deforms plastically.
[0045] Therefore, since the shearing stress in the case of [each] L character extrusion and the usual extrusion of two batches can be applied, crystal grain turns minutely further and the amount of preferred orientation improves. By making a cross section into a rectangle especially, the variation in the shearing stress in the cross direction of a dice can be abolished, and shearing stress can be equalized. Moreover, since the configuration of the outlet side of a dice 41 is a drawing configuration as mentioned above, it can restrain the material which comes out in response to processing from the outlet of a dice 41, and can prevent destruction (buckling) of material.
[0046] Next, the 6th operation form of this invention is explained. Drawing 7 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 6th operation form of this invention, and punch. The entrance-side path 55 in which punch 13 is taken in and out of the dice 51 of the extruding equipment concerning this operation form up and down, and two outlet side paths 57 and 58 in which mold goods are extruded are formed. The entrance-side path 55 and the outlet side paths 57 and 58 are open for free passage, and the outlet side paths 57 and 58 accomplished the angle of about 90 degrees to the entrance-side path 55, respectively, and are mutually prolonged in

opposite direction. Moreover, like the 1st operation form, the outlet side paths 57 and 58 are formed so that the cross section may decrease toward the outlet of a dice.
[0047] If thermoelectric material 20 is poured into the entrance-side path 55 and punch 13 is dropped, mold goods will be extruded from two outlet side paths 57 and 58. At this time, the two boundary sections X and Y which the entrance-side path 55 and two outlet side paths 57 and 58 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20.
[0048] In addition, although two outlet side paths 57 and 58 were established in this operation form so that the angle of about 90 degrees might be accomplished to the entrance-side path 55, respectively, you may establish three or more outlet side paths. Moreover, the angle of an entrance-side path and an outlet side path to accomplish has [that what is necessary is just to be in the larger range smaller than 180 degrees than 0 degree] the especially desirable range of 45 degrees - 135 degrees.
[0049] Next, the 7th operation gestalt of this invention is explained. Drawing 8 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 7th operation gestalt of this invention, and punch. The extruding equipment concerning this operation gestalt is equipped with three punch 12, 13, and 14. The entrance-side path 65 in which punch 13 is taken in and out of a dice 61 up and down, the outlet side path 67 in which punch 12 is taken in and out of right and left, and the outlet side path 68 in which punch 14 is taken in and out of right and left are formed. In a dice 61, the entrance-side path 65 and the outlet side paths 67 and 68 are open for free passage. The extrusion punch (extrusion tool) 13 for pushing on the entrance-side path 65 the material poured into this trajectory is formed so that this path may be slid. Moreover, the presser-foot punch (presser-foot tool) 12 which applies back pressure to the outlet side path 67 by pushing back the material extruded from this trajectory is formed so that this path may be slid. Similarly, by pushing back the material extruded from this trajectory, the presser-foot punch 14 to which back pressure is applied is formed in the outlet side path 68 so that this path may be slid.
[0050] In case thermoelectric material carries out extruding using a dice 61, while pouring thermoelectric material into the entrance-side path 65 and dropping extrusion punch 13, presser-foot punch 12 and 14 is retreated applying back pressure. At this time, the two boundary sections X and Y which the entrance-side path 65 and two outlet side paths 67 and 68 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20. Furthermore, since thermoelectric material 20 was pressed down in the outlet side paths 67 and 68 and has received high compressive stress from punch 12 and 14, the shearing stress in the boundary sections X and Y becomes strong.
[0051] Next, the operation gestalt of the octavus of this invention is explained. Drawing 9 is the side cross section showing the structure of the dice used in the extruding equipment concerning the operation gestalt of the octavus of this invention, and punch. The middle path 76 which connects to the dice 71 of the extruding equipment concerning this operation gestalt the entrance-side path 75 punch 13 is taken in and out of which up and down, the outlet side path 77 by which mold goods are extruded, and the entrance-side path 75 and the outlet side path 77 is formed. The angle which each path is opening for free passage and the entrance-side path 75 and the middle path 76 make is about 90 degrees, and the angle which the middle path 76 and the outlet side path 77 make is about 90 degrees. The cross-section configuration of each path is a square (preferably rectangle). Moreover, the cross section of the entrance-side path 75 and the cross section of the middle path 76 are equal. The outlet side path 77 is formed so that the cross section may decrease toward the outlet of a dice 71. That is, the outlet side path 77 contains converging section 77a to which the cross section decreases gradually from the free passage section with the middle path 76, and that the cross section's has decreased diameter reduction section 77b.
[0052] If thermoelectric material is poured into the entrance-side path 75 and punch 13 is dropped, a sintered compact will be extruded from the outlet side path 77 through the middle path 76. At this time, a shear zone strong against thermoelectric material 20 is added in a path open for free passage in two places, the boundary section X which the entrance-side path 75 and the middle path 76 open for free passage right-angled, and the boundary section Y which the middle path 76 and the outlet side path 77 open for free passage right-angled. Furthermore, since converging section 77a is formed in the outlet side path 77, also in this converging section 77a, external force is received [E] from the side, and thermoelectric material 20 deforms plastically. Therefore, it is possible to make crystal grain turn minutely further and to raise a stacking tendency. Moreover, since the configuration of the outlet side of a dice 71 is a drawing configuration as mentioned above, it can restrain the material which comes out in response to processing from the outlet of a dice 71, and can prevent destruction (buckling) of material.
[0053] Next, the 9th operation gestalt of this invention is explained. Drawing 10 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 9th operation gestalt of this invention, and punch. The middle path 86 which connects to the dice 81 of the extruding equipment concerning this operation gestalt the entrance-side path 85 punch 13 is taken in and out of which up and down, the outlet side path 87 by which mold goods are extruded, and the entrance-side path 85 and the outlet side path 87 is formed. The angle which each path is opening for free passage and the entrance-side path 85 and the middle path 86 make is about 90 degrees, and the angle which the middle path 86 and the outlet side path 87 make is about 90 degrees. The cross-section configuration of each path is a square (preferably rectangle). Moreover, the cross section of each path is small in order of the entrance-side path 85, the middle path 86, and the outlet side path 87. Furthermore, the outlet side path 87 is formed so that the cross section may decrease toward the outlet of a dice 81.
[0054] If thermoelectric material 20 is poured into the entrance-side path 85 and punch 13 is dropped, a sintered compact will be extruded from the outlet path 87 through the middle path 86. Since the cross section is decreasing as these paths go to the outlet side of material at this time, it is very effective for preventing buckling of material.
[0055] When an extrusion path has two or more bends as in the operation gestalt of the octavus, or the 9th operation gestalt especially, destruction of material can be suppressed by putting in dummy material at the nose of cam of thermoelectric material 20, and performing extruding.
[0056] Next, the 10th operation gestalt of this invention is explained. In the following operation gestalten, T character extrusion is performed using two punch. Drawing 11 is drawing showing the outline of the extruding equipment concerning the 10th operation gestalt of this invention. As shown in drawing 11 , extruding equipment 100 contains two punch 112 and 113 which extrudes the thermoelectric material 20 by which powder molding was carried out, and the dice 111 which is the metal mold which makes the thermoelectric material 20 extruded by punch 112 and 113 deform plastically. Punch 112 and 113 moves to right and left with the slides 101 and 102 driven with an actuator (oil hydraulic cylinder). The extrusion

pressure of punch 112 and 113 is measured by load cells 103 and 104, respectively, and the variation rate of punch 112 and 113 is measured by displacement gages 105 and 106, respectively. By acting as the monitor of the relation between the measurement value of displacement gages 105 and 106, and elapsed time, the drive of slides 101 and 102 is controllable so that punch 112 and 113 extrudes thermoelectric material 20 at an almost fixed extrusion speed.

[0057] On the base 107 in which the dice 111 is installed, the heater 108 for heating a dice 111 and thermoelectric material 20 is installed. By using a heater 108, it is possible to perform hot-extrusion processing. The temperature of a dice 111 is measured by the temperature sensor 109 arranged near the dice 111. By feeding back the measurement value of a temperature sensor 109 and controlling the calorific value of a heater 108, a dice 111 and thermoelectric material 20 can be maintained at desired temperature.

[0058] As for hot-extrusion processing, it is desirable in inert gas atmosphere, such as an argon, or a vacuum to perform extrusion speed as for example, 0.1 mm/min, keeping more desirable 350 degrees C - 600 degrees C of working temperatures at 420 degrees C - about 500 degrees C.

[0059] Drawing 12 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 10th operation gestalt of this invention, and punch. Two entrance-side paths 121 and 122 in which two punch 112 and 113 is taken in and out of right and left, respectively, and the outlet side path 123 by which mold goods are extruded are formed in the dice 111 of the extruding equipment concerning this operation gestalt. The entrance-side paths 112 and 113 and the outlet side path 123 are open for free passage. In this invention, it is required for the outlet side path 123 to accomplish a larger angle smaller than 180 degrees than 0 degree to the entrance-side paths 112 and 113, and it may be 45 degrees - 135 degrees desirably. In the following operation gestalten, the angle which makes this angle about 90 degrees, and the entrance-side paths 112 and 113 constitute is made into about 180 degrees.

[0060] If thermoelectric material 20 is poured in from the entrance-side path 121 or 122 and punch 112 and 113 is driven, thermoelectric material 20 will be equally pressurized from both sides, and mold goods will be extruded from the outlet side path 123. At this time, the two boundary sections X and Y which two entrance-side paths 121 and 122 and outlet side paths 123 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20. Thus, the orientation of the crystal grain in thermoelectric material serves as a bilateral symmetry to the longitudinal plane of symmetry of thermoelectric material by adding shearing stress equally from right and left.

[0061] Next, the 11th operation gestalt of this invention is explained. Drawing 13 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 11th operation gestalt of this invention, and punch. The entrance-side paths 131 and 132 in which two punch 112 and 113 is taken in and out of right and left, respectively, and two outlet side paths 133 in which mold goods are extruded are formed in the dice 130 of the extruding equipment concerning this operation gestalt. Like the 1st operation gestalt, the converging section 134 is formed in the outlet side path 133 so that the cross section may decrease toward the outlet of a dice.

[0062] If thermoelectric material 20 is poured into the entrance-side path 131 or 132 and punch 112 and 113 is driven, thermoelectric material 20 will be equally pressurized from both sides, and mold goods will be extruded from the outlet side path 133. At this time, the two boundary sections X and Y which two entrance-side paths 131 and 132 and outlet side paths 133 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20. Furthermore, if thermoelectric material 20 progresses to the outlet side path 133, external force will be received of the converging section 134 of this trajectory / E] from the side, and thermoelectric material 20 will deform plastically. The crystal grain which constitutes thermoelectric material turns minutely further by this, and the amount of preferred orientation improves.

[0063] According to this operation gestalt, both extrusion usually receives symmetrical shearing stress to the center line of thermoelectric material with T character extrusion. Therefore, over the whole interior of thermoelectric material, the orientation of a grain boundary is a bilateral symmetry and the thermoelectric material which does not have variation in the property of the organization by the position can be manufactured.

[0064] Next, the 12th operation gestalt of this invention is explained. Drawing 14 is the side cross section showing the structure of the dice used in the extruding equipment concerning the 12th operation gestalt of this invention, and punch. The extruding equipment concerning this operation gestalt is equipped with three punch 112, 113, and 114. The entrance-side paths 141 and 142 in which two punch 112 and 113 is taken in and out of right and left, respectively, and the outlet side path 143 punch 114 is taken in and out of which up and down are formed in the dice 140. The extrusion punch 112 and 113 for pushing on the entrance-side paths 141 and 142 the material poured into this trajectory from both sides is formed so that this path may be slid. Moreover, the presser-foot punch (presser-foot tool) 114 which applies back pressure to the outlet side path 67 by pushing back the material extruded from this trajectory is formed so that this path may be slid.

[0065] In case thermoelectric material carries out extruding using a dice 140, while pouring in thermoelectric material from the entrance-side path 141 or 142 and making extrusion punch 112 and 113 drive, presser-foot punch 114 is retreated applying back pressure. At this time, the two boundary sections X and Y which two entrance-side paths 141 and 142 and outlet side paths 143 open for free passage at a right angle mostly serve as a shear zone, and shearing stress is added to thermoelectric material 20. Furthermore, since thermoelectric material 20 was pressed down in the outlet side path 143 and has received high compressive stress from punch 114, the shearing stress in the boundary sections X and Y becomes strong.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the outline of the extruding equipment concerning the 1st operation gestalt of this invention.
[Drawing 2] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 1st operation gestalt of this invention, and punch, and (A) and (B) show two states under extruding.
[Drawing 3] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 2nd operation gestalt of this invention, and punch, and, in (A), (B) shows the state after punch press before punch press.
[Drawing 4] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 3rd operation gestalt of this invention, and punch, and (A) and (B) show two states under extruding.
[Drawing 5] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 4th operation gestalt of this invention, and punch.
[Drawing 6] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 5th operation gestalt of this invention, and punch.
[Drawing 7] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 6th operation gestalt of this invention, and punch.
[Drawing 8] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 7th operation gestalt of this invention, and punch.
[Drawing 9] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 8th operation form of this invention, and punch.
[Drawing 10] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 9th operation form of this invention, and punch.
[Drawing 11] It is drawing showing the outline of the extruding equipment concerning the 10th operation form of this invention.
[Drawing 12] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 10th operation form of this invention, and punch.
[Drawing 13] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 11th operation form of this invention, and punch.
[Drawing 14] It is the side cross section showing the structure of the dice used in the extruding equipment concerning the 12th operation form of this invention, and punch.
[Drawing 15] It is drawing which explains typically the manufacture method of the thermoelectrical semiconductor material currently indicated by JP,2000-124512,A, and, in (A), (B) shows the state after punch press before punch press.
[Drawing 16] It is drawing which explains typically the method currently indicated by reference "orientation control of the Bi-Te system material by the strong shear addition knockout", and, in (A), (B) shows the state after punch press before punch press.
[Description of Notations]
1,101,102 Slide
2,103,104 Load cell
5,105,106 Displacement gage
6,108 Heater
7,107 Base
8,109 Temperature sensor
10,100 Extruding equipment
11, 21, 31, 41, 51, 61, 71, 81 Dice
12, 13, 14, 23, 24, 33 Punch
15, 25, 35, 45, 55, 65, 75, 85 Entrance-side path
76 86 Middle path
17, 27, 37, 47, 57, 58, 67, 68, 77, 87 Outlet side path
20 Thermoelectric Material
111, 130, 140 Dice
112, 113, 114 Punch
121, 122, 131, 142, 141, 142 Entrance-side path
123, 133, 143 Outlet side path
134 Converging Section

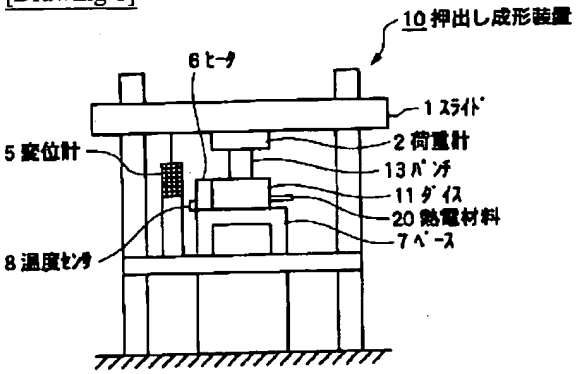
[Translation done.]

* NOTICES *

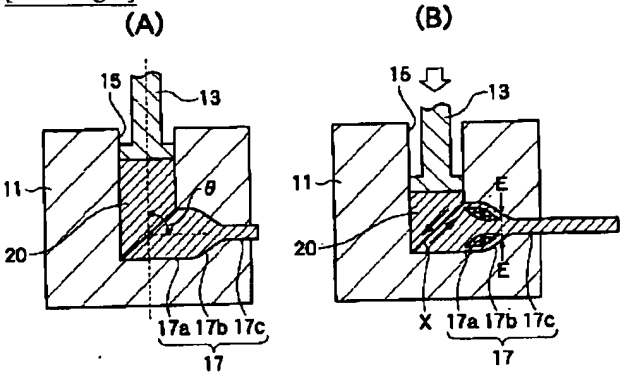
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

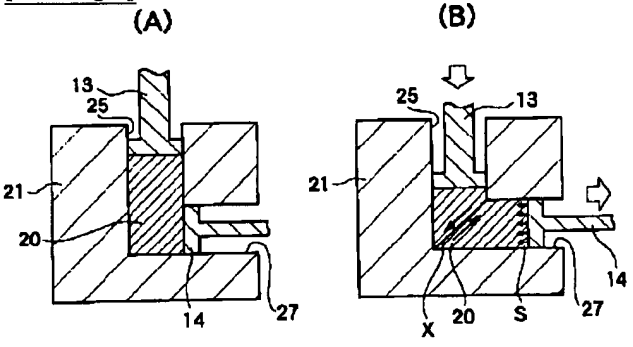
[Drawing 1]



[Drawing 2]



[Drawing 3]



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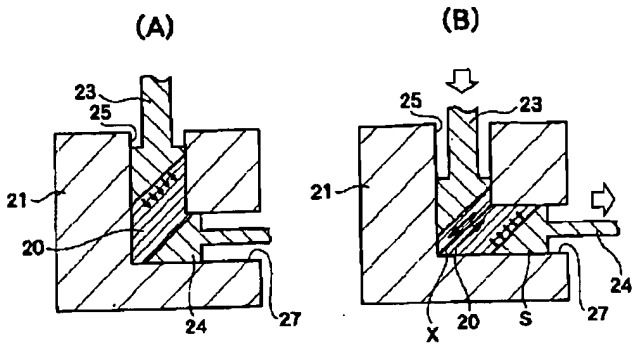

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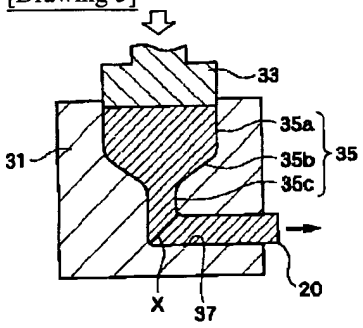

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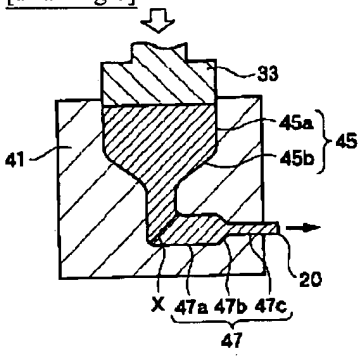

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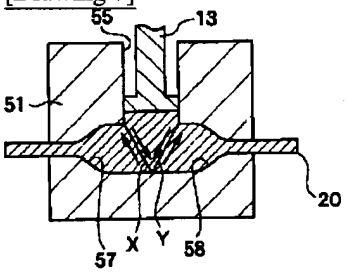

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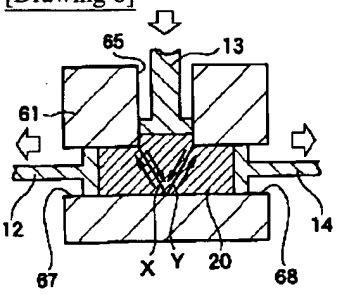

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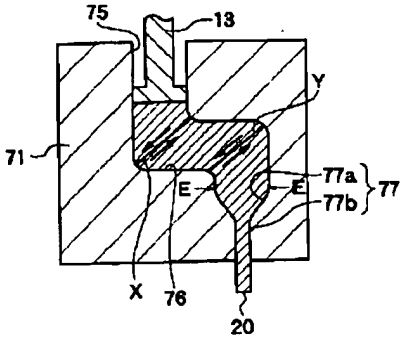

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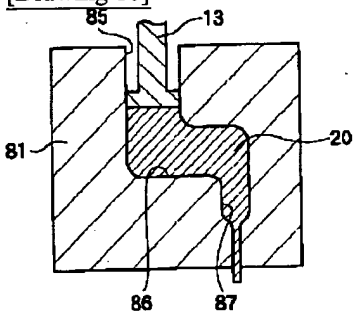

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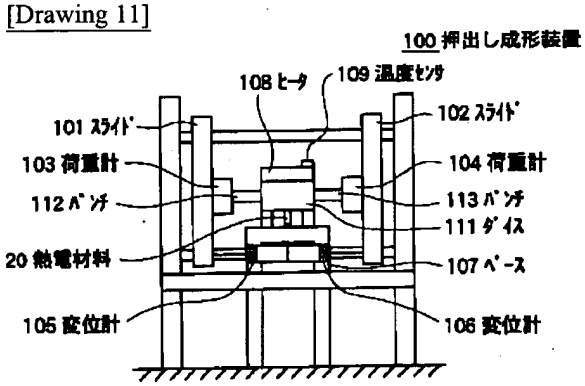

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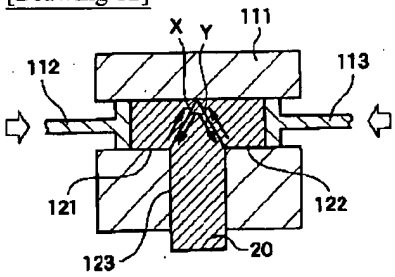
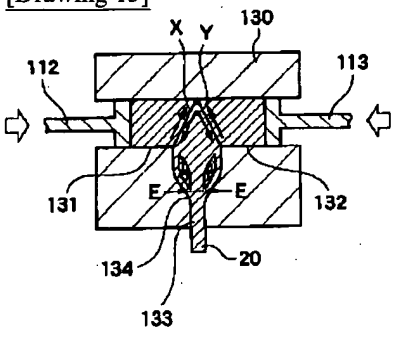


[Drawing 13]



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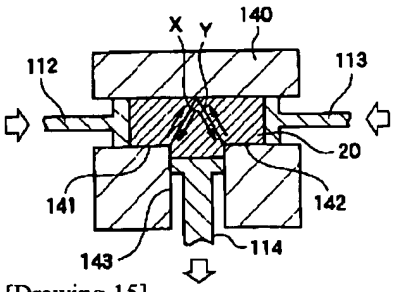

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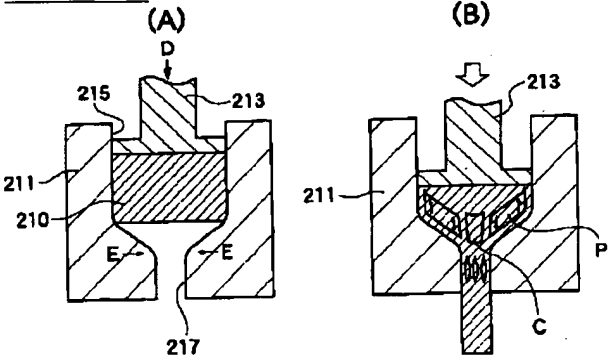

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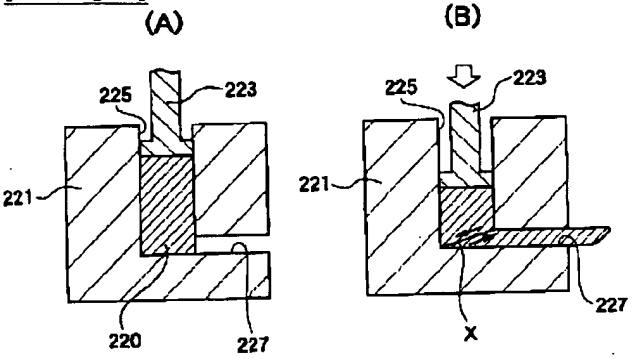

[Translation done.]